Author Response to D. Taraborrelli (Referee)

We thank Dr. Taraborrelli for taking the time to carefully review our manuscript and provide critical feedback and valuable insights. Our responses to questions and suggestions are outlined below. Most of the referee's comments concern the MCM or our alterations to it. We hope studies like this and comparisons to fundamental laboratory studies ultimately lead to the formal updating of the MCM, which is a valuable publically available tool. We agree with, and have implemented, all of Dr. Taraborrelli's suggestions. While there is a general improvement in the measurement-model agreement as a result, the changes were not large enough or not of a direction to impact our conclusions in this paper or the companion paper.

REFEREE:

Major Comments

Epoxide chemistry: The study of Butkovskaya et al(2006) provides some evidence for only 0.125 OH that results from the reaction of O2 with the HOCHCHO radical from HOCH2CHO reaction. For consistency, HOCH2CHO + OH reaction should be changed as well. In many reactions the HOCH2CO3 radical is produced. For consistency, HOCH2CO3 should be substituted with the HOCH2CO radical that undergoes decomposition upon reaction with O2 as quantified by Butkovskaya et al(2006).

RESPONSE:

Following Butkovskaya (2006), we alter the oxidation scheme for glycoaldehyde as follows. First, we have updated the product yields for the minor channel of OH + HOCH2CHO (that for abstraction of the center H):

 $OH + HOCH2CHO \rightarrow 0.81GLYOX + 0.81HO2 + 0.19HCOOH + 0.19OH$

Next, we implemented a fast unimolecular decomposition channel for the HOCH2CO3 radical:

HOCH2CO3 → 0.73HO2 + 0.84HCHO + 0.58CO + 0.26OH

Butkovskaya (2006) suggests that the latter reaction should be "very fast" but does not give a rate constant for decomposition of the peroxy radical. We implement this reaction with a rate constant of 10 /s. This reduces modeled HOCH2CO3 from 1.9 pptv to 0.01 pptv.

The tentative simplified dihydroxyepoxide chemistry by Paulot et al(2009a) is adopted. However, the reaction IEPOXO2 + HO2 unrealistically yields 1.125 OH. Furthermore, there is no experimental evidence (that I am aware of) for an OH-yield of 1 for the IEPOXO2 + HO2 reaction via a mechanism similar to the one for CH3CO3 + HO2. In fact, this was assumed "for simplicity" by Paulot et al(2009b) (F. Paulot, pers. comm.). A way out for the authors would be to assume that IEPOX + OH reaction proceeds via the mechanism described labeled as SR7c in the SOM of Paulot et al.(2009b). When considering the epoxide resulting from ISOPBOOH + OH the major products should be the peroxy radicals C57O2 and C58O2, already present in the MCM mechanism subset for isoprene. A similar choice was done by Archibald et al(2010). Though we did not specifically note it in the manuscripts, the IEPOX mechanism has very little effect on modeled OH, even with a yield of 1.125. Still, we agree that this yield is likely too high. While restricting IEPOX oxidation to the SR7c mechanism would remove this issue, it would potentially neglect other channels and may also require implementing new species. To maintain simplicity in the IEPOX mechanism, we modify it by replacing the formation of IEPOXO2 (and subsequent degradation) with the reaction

IEPOX + OH \rightarrow 0.5C57O2 + 0.5C58O2, k = 5.78 x 10⁻¹¹ exp(-400/T) cm³ molec⁻¹ s⁻¹

Though this is only strictly correct for the IEPOX derived from ISOPBOOH and ISOPDOOH, these two are the most dominant of the four MCM isomers. Moreover, as noted in the SOM of Paulot (2009), the fate of the epoxides evolving from ISOPAOOH and ISOPDOOH is less certain.

ISOPOOH + OH Reactions: Paulot et al(2009b) used two reaction channels for OH + ISOPOOH (sum of A, B, C and D isomers) with the corresponding estimated rate constants. One channel produces the epoxide and the other one recycles 30% OH and forms 70% of the original ISOPO2. If this simplified scheme is adopted, the MCM reactions

OH + ISOPAOOH ! HC4ACHO + OH 1.07 10–10 cm3 molec–1 s–1 OH + ISOPBOOH ! ISOPBO2 4.2 10–11 cm3 molec–1 s–1 OH + ISOPCOOH ! HC4CCHO + OH 1.07 10–10 cm3 molec–1 s–1 OH + ISOPDOOH ! HCOC5 + OH 1.07 10–10 cm3 molec–1 s–1

should not be considered any longer. From the text and Table 6 it looks like these reactions were kept and not replaced. Then the authors use the second channel by Paulot et al(2009b)

ISOPOOH + OH ! 0.70 ISOPO2 + .30 OH + 0.30 HC5

only for ISOPBOOH that ironically is the only isomer that cannot recycle OH that way. In this case the -OOH group is on a tertiary C atom with no H-atom to abstract. HC5 is likely what in MCM is called HCOC5 and it is related to ISOPDO2 and not to ISOPBO2. Furthermore, the authors retain the rate constant 4.2 10–11 cm3 molec–1 s–1 for this reaction that is unrealistically to high for this channel. The reaction channel

ROOH + OH ! RO2 + H2O

should be considered for each ROOH isomer and the corresponding rate constant should be similar to the one for CH3OOH that is $0.6 \cdot 5.3 \ 10-12 \cdot \exp(190/\text{temp})$ cm3 molec-1 s-1(IUPAC Data Sheet HOx VOC34). In fact, Paulot et al(2009b) used the expression 3.8 $10-12 \cdot \exp(200/\text{temp})$ cm3 molec-1 s-1 that is the previous IUPAC recommendation for CH3OOH + OH ! CH3O2 + H2O reaction. We have restored the modified reaction for ISOPBOOH to its original MCM form (i.e. not making OH and HC5). Also, we have updated the rate constant for the reactions ISOP*OOH + OH \rightarrow ISOP*O2 to the value of 0.6*5.3e-12*exp(190/T), following IUPAC recommendations for the analogous CH3OOH reaction.

This change results in a 57% increase in modeled ISOPOOH concentrations.

Monoterpene kinetics: In Table 6 an extension of MCM with partial chemistry of monoterpene and sesquiterpene is attempted. For both rate constants and product yields Atkinson and Arey (2003a) is cited although the rate constants were explicitly reported in Atkinson and Arey(2003b). This second source should be cited as well.

We have added this reference.

Regarding myrcene and α - terpinene reaction with OH, Hites and Turner(2009) and Peeters et al(1999) reported measured rate constants that are about 30% higher than recommended by Atkinson and Arey(2003b). Actually the latter goes back to Atkinson et al(1997).

We have updated these rate constants following Hites and Turner (2009).

Moreover, in Table 6 the rate constant of α -terpinene with O3 should be 2 10–14 (Atkinson and Arey(2003b)) and not 1.4 10–16 cm3 molec–1 s–1 as for γ -terpinene.

We have corrected this error.

In the companion manuscript the authors show that the model overestimates the mixing ratios of myrcene and alpha-terpinene and the new rate constants will significantly decrease the model-measurement discrepancy.

Indeed, this does improve model agreement with these compounds. Thank you.

The average acetone-yield from myrcene + O3 reactions should be about 25% and not 20% (Atkinson and Arey (2003a)). Why has a 20% yield been chosen?

This is a typo; our mechanism does use a yield of 25%. Thank you.

MBO chemistry: The MCM rate constant for the MBO + OH reaction has no temperature dependence and is about 10% higher than what recommended by IUPAC at 298K, 8.1 $10-12 \cdot \exp(610/\text{temp})$ cm3 molec-1 s-1. In fact, its rate constant should change by about 10% between cold and hot periods during BEARPEX. Considering that MBO is the most abundant VOC during BEARPEX contributing to the OH-reactivity the most, it is fair to expect a significant effect on the model results when the IUPAC recommendations are used.

We have modified this rate constant to match IUPAC recommendations. For the hot period when the discrepancy between old and new rate constants is largest—this reduces modeled MBO by 3%.

Minor Comments

In the manuscript the authors state that their model is the first of its kind to incorporate the Master Chemical Mechanism (MCM). I am afraid this is not true. I am aware of at least another model (SOSA) whose description manuscript has already received positive reviews in ACPD (Boy et al., ACPD 2010) and will likely published earlier than the present manuscript.

Thank you for bringing this paper to our attention. We have referenced this manuscript and adjust our statements accordingly.

In Sec. 3.7 and Tab. 6 the authors refer to Hasson et al(2004) for the 44% OH-yield in three RCO3 + HO2 reactions. However, the number 44% is the average OH-yield for the CH3CO3 + HO2 reaction studied in another two labs (Dillon and Crowley(2008), Jenkin et al(2007)). This average value is recommended by IUPAC (Data Sheet HOx VOC54). Although the authors do not mention the yields for the other two channels of RCO3 + HO2, I assume that they are as the ones recommeded by IUPAC, that is 15% and 41% for the RCO2H + O3 and RCO3H channels, respectively. For the sake of clarity, it would better to mention all of this in the manuscript.

We have changed the reference for this yield to IUPAC.

The referee is correct in that we have also updated the other reaction pathways, though this is not clear in the text. We have altered the text and table to clarify our modifications.

In Section 3.9 little is mentioned about the chemistry operator. I wonder in which format the MCM subset was downloaded. Considering the significant modifications to the mechanism, I imagine the format is probably the user-friendly format used by Kinetic Pre-Processor (KPP) (Sandu and Sander, 2006). Was this the case?

No. We download the MCM subset in the FACSIMILE format and parse the raw text file to generate computer code. The entire model is written and executed in MATLAB, including code which effectively generates the Jacobian automatically from the FACSIMILE text file. In other words, each reaction and mass balance equation is not coded by hand but by MATLAB code. We have added these details in the text.

Suggestions for Further Changes

In light of the use the authors make of the CAFE model (see companion manuscript), the following suggestions for changes to the chemical mechanism may significantly improve the model results.

Alkyl nitrates: Paulot et al(2009a) determined 11 and 15% yield for the alkyl nitrates from MVK and MACR OH-initiated oxidation. The MCM considers only a very small yield for

the minor RO2 isomer resulting from the MVK + OH reaction. A simplified chemistry for these two alkyl nitrates couldbe taken from Paulot et al(2009a). Inclusion of the new alkyl nitrate yields may significantly improve the underestimation of the alkyl nitrate as shown in the companion manuscript.

We have modified the mechanism as follows:

- 1) Updated the yield of HMVKANO3 from 0.017 to 0.11
- 2) Altered the reaction of MACRO2 +NO to include a 15% yield of a new species, MACRNO3. The yield for the other channel is reduced to 85%.
- 3) Based on Paulot et al. (2009, ACP), added the reaction MACRNO3 + OH \rightarrow 0.08(CH3CO2H + HCHO + NO3) + 0.07(HCOOH + MGLYOX + NO3) + 0.85(ACETOL + NO2), k = 5x 10⁻¹¹ cm³ molec⁻¹ s⁻¹

These changes lead to a 12% increase in total modeled ANs for the hot period.

CH3CO3 production and PAN: According to Baeza-Romero et al.(2007) the CH3CO3 yield from MGLYOX + OH reaction is 0.6. Furthermore, the study by Orlando et al(1999) suggests that the degradation of methyl-vinyl radical (represented in MCM by the decomposition reaction of MACO2) produces only 0.35 CH3CO3 under high-NOx conditions. LaFranchi et al(2009) took it into account in their PAN budget analysis for BEARPEX 2007. In the companion manuscript the authors state that PAN is overestimated by 60% during hot days and this may help in reducing the discrepancy. Finally, the rate constant for the PAN + OH reaction in MCM is about 3 times higher than the upper limit recommended by IUPAC (3 10–14cm3 molec–1 s–1).

We have modified the mechanism as follows:

- 1) MGLYOX+OH \rightarrow 0.6(CH3CO3 + CO) + 0.4(CH3O2 + 2CO)
- 2) MACO3 + NO \rightarrow 0.35(CH3CO3 + HCHO + NO2) + 0.65(CH3O2 + CO + HCHO + NO2)
- 3) The rate constant for PAN+OH is increased to 3×10^{-14} .

These changes decrease modeled PAN by 4% in the hot period.

MBO chemistry: 2-hydroxy-2-methylpropionaldehyde (IBUTALOH) is a major product of MBO oxidation. Its chemistry has been studied by Carrasco et al(2006) and it is quite different from the one implemented in MCM. First of all the IUPAC recommendations (Data Sheet HOx VOC33) for the rate constant of IBUTALOH + OH is 36% lower than in MCM. Second, the PAN-like compound, called C4PAN5 in MCM (Table A1), could not be detected. This agrees with theoretical predictions of Mereau et al. that the potential precursor of C4PAN5, the excited acyl radical resulting from IBUTALOH + OH, decomposes losing a CO molecule. Therefore, C4PAN5 is likely not formed during MBO degradation. In my opinion the IPRHOCO3-related species should not be present in the mechanism. This has significant implications for the overestimation of the total peroxyacyl nitrates showed in the companion manuscript.

We have modified the mechanism as follows:

- 1) The rate constant for IBUTALOH is set to the IUPAC value of 1.4e-11
- 2) The IPRHOCO3 molecule is allowed to unimolecularly decompose by a mechanism similar to the Butkovskaya (2006) glyoaldehyde mechanism:

IPRHOCO3 \rightarrow OH + CH3COCH3 + CO2, k = 10 s⁻¹

We choose the acetone yield to be 100% (e.g. no *cis*- O_2 channel) to stay consistent with the results of Carrasco et al. (2006).

These changes reduce modeled C4PAN5 from 36 to 0.2 pptv and reduced total APNs by 4%. We have already noted in the text that we were unable to detect C4PAN5 in the TD-CIMS measurements.

Technical corrections: p.21653, l.17: "affect" should be "effect"

Fixed.

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