

We would like to thank the reviewers for their helpful and positive comments which have improved the paper. The specific comments of the reviewers are in bold below together with their responses.

Referee #1

Constraint of CH₂O: Because the oxidation of VOCs flows through CH₂O on the way to radical and O₃ production, the constraint of CH₂O to observations effectively shortcircuits the chemical cycling in a model. An argument can be made for constraint of CH₂O for budget purposes, such as in Figures 7 and 9. However, for sensitivity analyses, such as for Figure 9 and accompanying discussion, CH₂O must certainly be allowed to vary with changing VOC concentration. It is unclear from the paper whether CH₂O is model-calculated for these sensitivity runs. Discussion of the single point or modeling (line 17 p. 17045) indicates specifically that CH₂O is constrained. Discussion in Section 5.2, line 21 p. 17046 indicates that isoprene and NO_x are varied “. . .while maintaining all other species at their observed levels (Table 3).” However, Table 3 does not list CH₂O as a constraining species. I suspect that the authors conducted the simulations appropriately and did not constrain CH₂O and other aldehydes, and that this simply needs to be stated in the discussion. If this is not the case, then the simulations need to be run without constraint of CH₂O and other aldehydes. For the overall analysis, it might be worth running the model with CH₂O unconstrained and see if there is much of an impact on overall results.

This was unclear. As the reviewer suspected the sensitivity runs for Figure 9 and accompanying discussion are unconstrained to HCHO and other isoprene degradation products. We have added ‘Model runs described here were unconstrained to HCHO and isoprene degradation products’ to the figure caption of Figure 9 for clarity.

Figure 9: This figure is not intuitive and is quite confusing. It is described in the text (lines 22-26, p. 17046) as “. . .showing the effects of increasing isoprene concentration under different isoprene and NO_x regimes.” However, the only way I can make sense of the Figure is that it shows the effects of *decreasing* isoprene concentration. The caption indicates that it shows HO₂ relative to a run where isoprene has been increased by a factor of ten, suggesting that this latter interpretation is correct (and is consistent with the later figure discussion). My preference would be to show the change in HO₂ due to increasing isoprene. However, whichever way the authors choose, it needs to be clearly described.

We have updated the figure caption for clarity to ‘... relative to a run where the isoprene concentration was a factor of ten lower ...’.

The discussion of the low NO_x regime 10-50 ppt (top of p. 17047) concerns me. The discussion describes this regime as where HO₂ decreases with increasing isoprene concentration (indicated by the yellow/orange colors on the Figure). No mention is made of the blue shades within this NO_x regime at the highest isoprene levels at the top of the plot however, and in fact, the average GABRIEL point (red diamond) falls into this area. The blue shades indicate increasing HO₂ with increasing isoprene, which

seems inconsistent with discussion of GABRIEL (line 14, p. 17048) “Under these conditions, peroxide production will be a significant sink for HO_x in the model.” Later, in the discussion of the very low NO_x (< 10 ppt), the blue colors at the highest isoprene concentrations are described as due to CH₂O from ozone reactions with isoprene. From this discussion alone, I would conclude that GABRIEL conditions are also affected by these conditions. Some clarification here is required.

For clarification we have removed that sentence and added ‘At the lower NO_x and higher isoprene concentrations observed during GABRIEL the modelled HO_x will be more sensitive to changes in isoprene than for AMMA’.

MINOR POINTS:

Abstract: Might be helpful to include median NO level (3-500 ppt is a large range).

Median NO level will be added to the abstract (76 ppt).

Introduction (paragraphs beginning line 26 p. 17033): Because this study is limited to analysis of HO₂, it would be helpful to include a few sentences describing the HO₂ obs/calc ratio under high isoprene conditions during INTEX-NA and GABRIEL. For example, Section 5.1, line 22 p. 10744 compares HO₂ obs/calc during AMMA to that in GABRIEL, so it would be helpful to outline HO₂ results from GABRIEL in addition to outlining the OH results.

Page 17034, line 6 the following will be added: ‘Observations of HO₂ were also found to be higher than model predictions during GABRIEL, although not to the same extent as for OH. At the highest isoprene concentration observed (~ 6 ppb) the modelled HO₂ was a factor of approximately 10 too low, compared to a factor of approximately 20 for OH.’

Model approach (line 22 p. 17039): How important are the HO₂ and OH losses to aerosol relative to other budget terms? Are they significant at all? (they are not mentioned in budget discussion.)

Losses due to aerosol were minimal, representing less than 1.5 % of the total loss for HO₂ and less for OH. We include this comment in the text on page 17049 line 26.

Table 2: Range of NO listed as .3-500 ppt (typo?)

The range is correct for the entire dataset. The range quoted earlier in the text is for the boundary layer.

Section 5 Figure 5 The simple PSS model/obs figure seems to indicate two branches - one that falls along the 1 line, and another that falls above. Can these be discriminated with respect to geography? (i.e., I would suspect the points where simple PSS model gives good agreement are desert)

The regimes do correspond to regions with low isoprene vs high isoprene, but include a mixture of boundary layer and free troposphere data points over both forest and desert. We include the following sentence in the Figure caption - 'While the apparent separation of the data into two regimes does correspond to data points with high isoprene and those with low isoprene, discrimination on the basis of geography is not possible since both regimes contain a mixture of boundary layer and free troposphere data points over both forest and Sahel.'

Section 5.1, line 22 p. 10744: Isoprene concentrations were much higher in GABRIEL than during AMMA. How do HO₂ obs/cal compare for comparable isoprene levels?

Page 17045, line 2 add the following: 'a ratio observed to modelled HO₂ of approximately 7 was observed in the boundary layer in the afternoon, with a ratio between 3 and 5 at isoprene concentrations comparable to those observed during AMMA (Kubistin et al., 2008).'

Section 5.1 line 4 p. 17045: This is semantics, but you shouldn't describe the point as "typical" when it was chosen because it has higher isoprene and lower NO than most of the data during AMMA. You chose this point for a good reason, but not because it is "typical".

Page 17045, line 5: 'Typical' will be removed.

Section 5.1, line 11 p. 17046: I suggest rewording the section where you state "isoprene has little impact on HO_x." I understand you intend to state that it has little impact on the total concentration of HO_x, but it does have a significant impact on HO_x partitioning.

Page 17046, line 11: Given the difficulty in making comparisons between the modelled and observed OH for this work the section will be altered to refer to HO₂ instead of HO_x.

Figure 9 caption "Model discrepancies observed during INTEX-A were found for isoprene > 2 ppb, but the corresponding NO concentration is not given (Ren et al., 2008)." These data are available on public archive (<http://wwwair.larc.nasa.gov/missions/intexna/intexna.htm>) Note that there are only 35 points (2% of the BL data) during INTEX-A where isoprene was larger than 2 ppb, but for those points, median NO was 22 ppt (and median HO₂ obs/cal = 2.4). This is consistent with your interpretation, so would be worthwhile citing.

The INTEX-A data will be included in the figure.

For the Figure 9 issues I brought out in my review, it may be worth checking on how sensitive the results are (in the very high isoprene, very low NO regime) to your constraint of O₃. You describe the increase in HO₂ with increasing isoprene as due to O₃+isop, leading through CH₂O to HO_x. It might be worth

checking on what O₃ concentrations were observed during GABRIEL, and how sensitive your results are to the concentration of O₃ you're constraining to, to help discover why the GABRIEL average is in the increasingHO₂ w/ increasing ISOP regime.

The following has been added to page 17048 line 10: 'These concentrations are marked on Fig. 9, and compare to (2000±760) ppt isoprene and (20±20) ppt NO for the GABRIEL campaign (Lelieveld et al., 2008), also marked on Fig. 9, although it should be noted that differences in ozone and CO concentrations between AMMA and GABRIEL and INTEX-A may contribute to the placement of the different campaigns in different chemical regimes.'

Referee #2

Despite the recent advancements in isoprene oxidation mechanisms and problems in reproducing many HOx measurements, it seems that a fortunate combination of conditions make possible that the isoprene mechanism in MCM, nearly unchanged for 12 years (Jenkin et al., J. Atmos. Chem. 1998), could reproduce HO₂. The new mechanism proposed by Peeters et al., PCCP (2009) still awaits experimental confirmations. In the meanwhile, what is shown in Fig. 8, the reaction ISOPOOH + OH → ISOPO, does not correspond to neither what standard VOC oxidation knowledge would suggest nor to what is in the MCM. In the latter the isomer ISOPBOOH reacts with OH giving solely ISOPBO₂ at a rate that is about 10 times higher than the actual H-abstraction from the -OOH group. ISOPBO₂ is the major RO₂ isomer from isoprene. The other three ROOH isomers recycle OH entirely upon reaction with OH and produce longlived carbonyl species and not alkoxy radicals. None of the ISOPOOH isomers produce HO₂ upon reaction with OH. Overall, this may lead to misunderstandings and confusion for the reader that is not familiar with MCM.

ISOPOOH + OH → ISOPO had been included in Figure 8 in error and has been removed. We apologise for the confusion.

In Fig. 7b the third and the fourth most important loss for HOx are the ISOPO₂ + HO₂ and ISOPBOOH + OH reactions. However, the latter reaction produces additional ISOPBO₂ radicals that will artificially enhance the loss of HO₂ due to ISOPO₂ radicals. This aspect of the model should be mentioned as it may have an effect opposite to the calibration issues for J(O₁D).

It is not clear to the authors why the reviewer considers the production of ISOPBO₂ from ISOPBOOH + OH to lead to an artificial enhancement of HO₂ loss. This may relate to the previous error and has been dealt with.

For further clarification Fig. 8 could be changed but I don't know how this could be possible for such a simplified diagram. Probably, either in the captions or in the text it could be specified that the MCM chemistry of the hydroperoxides from isoprene does not consider OH-addition to the double bonds and this is a source of uncertainty for the present assessment.

This will be added to the caption.

Minor comments

p 17041 l 2: 24 -> 24h

Caption Fig. 10: instead of "forest" it should be "Sahel"

'Forest' will be changed to 'Sahel'.