

We thank the referee for the constructive critical review, our response and changes are listed as follows:

General comments:

1. Throughout, PTR-MS (and PTR-ToF-MS) measurements of MVK and methacrolein (MACR) are used. There is a known interference in the MVK+MACR detection caused by ISOPOOH (Rivera-Rios et al., 2014). This could especially impact the observed diurnal cycle in Fig. 5h, given the timing of ISOPOOH growth shown in Fig. 8. Has this interference been accounted for (I don't see any mention in the text). If not, it should at least be discussed, but better yet would be to present a range for the measurements, with different assumptions about how strong the interference is.

Response:

This is a very good comment, thanks for pointing this out. To evaluate the interference of ISOPOOH on MVK+MACR, we carried out laboratory experiment to quantify its conversion rate. See Supplement Sect. 2 for detailed descriptions. We added a discussion about the interference of ISOPOOH on MVK+MACR in Sect. 5.

Changes:

Line 325-370 are added.

2. There is some focus in the text and the analysis on O₃, but this comes as a bit of a shock because it is not mentioned in the title, abstract, introduction, or conclusions. Why not? If the ozone budget analysis stays in the paper, it should at least be mentioned in the abstract, introduction and conclusions. Ideally, it would be nice if its inclusion were more closely tied to the isoprene work. As it stands now, the relevant text/figure just seem unrelated to the rest of the paper but nonetheless interesting).

Response:

Discussions on ozone analysis are added to the abstract, introduction, and conclusion.

Changes:

Line 15, 654 are added.

3. NO_x flux and ISOPN yields. The different values used (NO_x flux 5-30, yield 6-12%) represent a very large range, and there needs to be more discussion of this in the text. In particular, I think Fig. S8 should be brought into the main text, and also made easier to read/interpret (i.e., how about solid/dashed/dotted to represent one parameter and colors to represent the other). The figure neatly shows that for most species (exception ISOPN), the choice of parameter has a smaller impact on the simulation than the existing measurement uncertainty. For ISOPN, a more nuanced discussion is also needed. The ISOPN yield used here is on the extreme low end of the range found by Xiong et al. (2015), and much lower than used in the GEOS-Chem simulation that theoretically provides the basis for this model (Mao et al., 2013). Both Xiong et al. (2015) and Wolfe et al. (2015) found an extra ISOPN sink was needed (although disagree on what that might be). A higher yield (and possible extra sink) here would make this work more consistent with the recent literature. I also think it would make this work more self consistent – if the simulation is overestimating peak NO at 7am, surely ISOPN should also be overestimated at the same time – as seen in the simulations run with 9-12% yield.

Response:

We merged Figure S8 to Figure 5 as suggested. We also added comparison of HCHO to Figure 5, which is recommended by the other reviewer. We didn't use different color/line style combination to distinguish the sensitivity analyses results because most of the lines are very close with each other, doing so will make it harder to tell the lines from each other.

Specific comments:

1.

31625, final paragraph: These details about terminology don't seem relevant to the introduction. To some extent, NO:HO₂ is just another metric with arbitrary "low" and "high" values (beyond the "balanced situation at 1). Where do you draw the line? I understand why this is a more useful metric, but I don't think it's clear or relevant yet at this stage in the paper, and I suggest moving this discussion to the section where it is actually used (6.4). Also, I don't understand what is meant by the sentence "Second, HO₂, RO₂, ... are not explicitly represented..." You mean, just in the nomenclature? They are still influencing what happens in different regimes.

Response/Changes:

We moved this discussion to Sect. 6.4. In “Second, HO₂, RO₂, ... are not explicitly represented...”, we mean in the nomenclature. We deleted this sentence due to its ambiguity nature.

2.

31629, 23-25: As written this is somewhat misleading because Fig. S1 only shows profiles for 1 day. If this day is representative of other days this should be mentioned at least in the figure caption.

Response/Changes:

We added vertical profiles collected on 2013-6-4, 2013-6-12, and 2013-6-13 to Figure S1. The data show that the CBL was well-mixed during these sampling days. These vertical profiles are representative of the other days during this study and this is added in the figure caption.

3.

31630, 18-19: Derived from where? From observations or from an external model?

Response:

Large-scale meteorological forcings were estimated based on both observation and reanalysis models.

Changes:

None.

4.

31630, 19: What is meant by “species segregation” here?

Response:

The mixed-layer model used in this study assumes the CBL is well mixed. However, in reality, the turbulent mixing may not be able to mix the emitted VOC species uniformly inside the CBL. This may create sub-region where the VOC species are non-uniformly distributed.

Changes:

None.

5.

31631, 1-5: This is one place where more information is needed to understand what was done. Looking at Fig. S2, it's clear why the 7th wasn't included, but less clear what is wrong with the 9th. What does "consistency of O₃-NO_x-VOC diurnal profiles" mean, and how was that determined? How much tolerance was allowed?

Response:

We updated Figure S2 and added O₃ mixing ratio profiles. We added specific metrics which we used to choose the sampling days used in this study.

Changes:

Line 240-244.

6.

31632, 2: "depending on different conditions" is too vague – what were the most important factors influencing this?

Response:

We revised this and added detailed factors (meteorological condition, e.g., rain) to the main text.

Changes:

Line 266.

7.

31632, 7-22: NO_x flux is assumed to be entirely from soil. Is there no influence from nearby anthropogenic areas? Could anthropogenic sources help explain why you need a larger NO_x flux later on when you included more detailed chemistry?

Response:

In this study the sampling area is under fair anthropogenic influence. In the prescribed NO_x flux, source is not simulated explicitly. The higher NO_x flux used in the complex scheme could be partly attributed to anthropogenic source.

Changes:

None.

8.

31632, 24 – 31633, 7: This paragraph starts by saying *both* chemical schemes are a subset from MOZART, but then goes on to say the second one is actually from GEOSChem (which is a separate model) – that first statement needs to be removed.

Response:

The O₃-NO_x-HO_x chemistry in both chemical schemes are obtained from the MOZART chemistry module. In the complex scheme, we extended its chemistry with a subset from the GEOS-Chem (isoprene chemistry). So the complex scheme is a combination of a subset of MOZART (O₃-NO_x-HO_x chemistry) and a subset of GEOS-Chem (updated isoprene chemistry).

Changes:

Line 289, 294.

9.

31633, 10-16: Is this meant to be a list of things that characterise the complex scheme in GEOS-Chem v9-02, or things that are different between this implementation and the version in GEOS-Chem? If the former, 3 isn't right, because Mao et al. (2013) do include isoprene + NO₃ reaction. If the latter, this should be rewritten to clarify what is meant here.

Response:

Here item 1, 2 are the same as in GEOS-Chem; item 3, and 4 are different from GEOS-Chem.

Changes:

Line 300-305.

10.

31633, 25-26: Rather than R09, etc. it would be much clearer to list the actual species (especially since this table is in the SI, not in the main text!).

Response:

We added the three species involved in the photolysis reactions to the main text.

Changes:

Line 313-314.

11.

31633, 26: I don't understand the reference to Fig. S6 here – S6 only shows O₃, which is not one of the species outside the 20% range.

Response:

This is a typo here. "Figure S6" should be in "The relationship between solar zenith angle (sza) and photolysis rates (j) are obtained by performing curve fitting to an empirical function $j = a \times$

$\exp(b / \cos(\text{sza}))$, where a and b are two parameters obtained through curve fitting (Table S4 and Figure S6).” to show an example of the curve fitting result.

Changes:

We moved the reference to “Figure S6” to the sentence shown above.

12.

Section 4: Seems like this belongs right after the Experimental section (so it would be 2. Experimental, 3. Data Processing, 4. Mixed Layer Chemistry Model)

Response:

We moved the Data processing to Section 3 as recommended.

13.

31636, 18-19: Need to clarify that these profiles are from a different date and location! There are various things that could influence the changes seen in these profiles besides just the time difference. While the time difference is a compelling factor, it is highly misleading to imply (as is done in the text) that this is only showing diurnal variation. I think this point should also be made in the caption to Fig. 5.

Response:

We added clarifications about the fact that these profiles are from different days and different locations.

Changes:

Line 394-397. Page 30 Figure 5.

14.

31636, 24-26: Presumably this is the combination of the mixing (mentioned) and OH oxidation (not mentioned)?

Response/Changes:

We added OH oxidation as a factor to the text at Line 394.

15.

31637, 19-21: Another place where it is not clear what was actually done. How were these variables adjusted? Was it ad hoc to get the best fit to BLH growth rate? Given Table 2 shows an observed value for the BL potential temperature, can I assume it's actually just the FT potential temperature that was adjusted?

Response:

BL potential temperature is obtained from measurement. FT potential temperature was adjusted to get the best fit of BLH.

Changes:

None.

16.

31639, 9: "faster photolysis rates" than what? How much faster? How small was the impact?

Response:

We added the photolysis rates for MVKN and MARCN in the text. We also added the change in different photolysis rates of MVKN and MARCN.

Line 464-466.

17.

31641, 16-20: Another place where more detail is needed. Are these using observed or modeled values? How are Sprod and Sloss calculated? What is S's versus S'h? This is an important result so needs more basis.

Response:

We re-write the eqn 1 to make it easier to understand.

Changes:

Line 534-540.

18.

31642, 1: How is the 6% loss to ozone calculated? Is this from the model?

Response:

This result is obtained from the model output.

Changes:

None.

19.

31642, 28: If the chemistry term is mainly controlled by O3 photolysis, why is it net positive? What is the role of isoprene chemistry in this (nominally the topic of the paper)?

Response:

(1) There is a typo here, the chemistry term is mainly controlled by photolysis of the O3-NOx system. Positive O3 is sustained by the photolysis of NO2.

(2) As stated in the previous comment, ozonolysis of isoprene plays a small part (6%) as compared with OH. O₃ mainly affect isoprene chemistry indirectly through the O₃-NO_x-HO_x system, where NO_x and HO_x have more impact on the isoprene concentration.

Changes:

Line 568.

20.

31643, 2-3: Does the inverse relationship between deposition & chemistry simply reflect the fact that if more is produced near the surface, more will be deposited?

Response:

According to the deposition term $V_d \langle S \rangle$ in the updated version of eqn 1, higher $\langle S \rangle$ will induce higher deposition. However, production rate is not linearly correlated with the mixing ratio (turbulent mixing also play a part in affecting the variation of mixing ratio).

Changes:

None.

21.

31643, 10-14: For this discussion it would be really useful to refer to the diurnal cycle in Fig. 8. It would also be useful if the NO:HO₂ line in Fig. 8 was on a log scale.

Response:

We added reference of Figure 8 to this part. We changed the x-axis of Figure 8 to log-scale. However, we think changing to log-scale will make it harder to interpret since all other three variables are still in linear-scale. We will leave this to editor/reviewer to decide which version is better.

22.

31643, 22-23 & Fig. 7: Another place where more detail is needed. How is Fig. 7 calculated? Is this based on the diurnal cycle plots, pulling out values at appropriate ratios (and if so, with what temporal resolution?)? Or is this several runs of the model, at different fixed NO:HO₂ ratios? Or something else? On the figure, the x-axis should be clearly marked as starting at 1 (it looks like 0 which begs the question as to why there is any NO contribution at all). It would be nice to see a zoomed in version from e.g. 0-10, since this is where the behavior is actually changing.

Response:

Figure 7 is obtained from the output of a single model run of the MXLCH with complex scheme (Yield_{ISOPN}=6%, F_{NOx}=+/-30 ppbv m s⁻¹).

Changes:

We added detailed description of the data source in the caption of Figure 7. x-axis is changed to log-scale to make it easier to read.

23.

31644, 1: Why is CH₃(O)OO the dominant candidate? Is that just an output from the model, or something expected from literature?

Response:

There is a typo in the manuscript as pointed out by the other reviewer. CH₃(O)OO should be CH₃C(O)OO for acetyl peroxy radical. This result is based on the model output. There is still large uncertainty in the RO₂ channel as the fate of ISOP₂OO in the literature.

24.

31644, 6-7: Biggest difference is in the role of isomerisation. Are they both using the same isomerisation rate from Crounse? Should be specified.

Response:

Both study used the isomerization rate coefficient from Crounse et al, 2011.

Changes:

We added the reference to the isomerization rate coefficient in the text at Line 607-608.

25.

31644, 10-24: What is the dependence in this paragraph of the results on the choice of yield?
Would a higher yield (see earlier comments) change the results?

Response:

Sensitivity simulations on two other different ISOPN yields at 9 and 12% overestimate the ISOPN mixing ratios by 30 and 70 %, respectively at 10:00 CST (Figure 5f).

26.

31645, 22-24: This is true for isoprene, but not for monoterpenes (which are included in this sentence) – at least not consistent with the monoterpenes profile in Fig. 3.

Response:

Vertical profile of monoterpenes in Figure 3 during 10:06 CST show a mixing ratio of 0.50 ppbv near the surface, and 0.20 ppbv near the top of the CBL. We think this should be qualified as a gradient. The x-scale in Figure 3c does make the gradient seem insignificant, we added the mixing ratios listed above to the text in Sect. 5 to make it clear.

Changes:

We added the mixing ratios of monoterpenes during 10:06 CST in Sect. 5.

27.

Acknowledgements: Seems like a lot of the modeling relies on mechanisms made publicly available by the GEOS-Chem and MOZART groups – worth an acknowledgement perhaps?

Response:

We agree with the reviewer and added the acknowledgement as suggested.

28.

Fig. 5: Need to make it clear that the “diurnal” variation measured from the WASP system represents different days / flights. I know this is stated elsewhere, but it needs to be made explicit here for those who don’t do a careful reading. I don’t think it’s a problem, but there are other things besides diurnal variation going on for those species and readers need to be aware of that.

Response:

We agree with the reviewer and made changes accordingly.

Changes:

We added to the caption of Figure 5 with the information saying that the WASP data are from different days/RFs.

Technical corrections

Response:

Corrected as suggested.