

Response_acpd-15-C10529-2015:

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-NO_x 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 ISOPOO in the literature.

24.

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

Response:

Both study used the isomerization rate coefficient from Crouse 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.

Response_acpd-15-C11186-2016:

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

General comments:

1. Figure 3 suggests strong gradient of isoprene at noontime, from 4 ppbv at 200 m to 1 ppbv at 1200 m. While the MXLCH model agrees well with averaged values from WASP system and NCAR C-130 aircraft (Figure 5), the comparison for ISOPN, NO_x, and OH is in fact between surface observations on the tower and modeled bulk values within the whole CBL. I would expect some difference between surface observations and modeled bulk values for these species. Some caveats should be given here on comparing these species.

Response:

We are aware of the fact that when comparing ground-based measurement with the model bulk values, one should expect to see some difference. The difference, however, depends on the chemical lifetime of the species as well as the turbulent mixing time scale. For species with chemical lifetime comparable to turbulent mixing time scale (e.g., O₃), aircraft observations are within the uncertainty range of ground-based observation (Figure 5a). For species with shorter chemical lifetime (e.g., NO_x, HO_x), there are larger deviations between ground-based and aircraft observations. The MXLCH output using the complex chemical scheme agrees better with the aircraft observation for NO₂ (Figure 5c). Ground-based observation of OH concentration show large variations due to its short lifetime inside the CBL. Model output agrees well with the observation during noontime, relatively large deviation still exists during early morning. For ISOPN, please see the response in the next comment.

Changes:

Line 434-436. We added a sentence to stress the fact that ground-based observations are used in comparison with the model bulk output.

2. I am impressed by the good agreement between observed and modeled ISOPN. But I think the authors should provide more details on this comparison.

For observations, what is the observed ISOPN? Does it include all daytime C5 hydroxyl isoprene nitrates? Or just some isomers? Is there any nighttime isoprene nitrates being measured here?

For model, the authors show a short lifetime of ISOPN, but it seems to me that it is mainly due to a fast ozonolysis rate, which has been suggested to be much slower from recent lab data. How would that impact their results? There has been discussion on hydrolysis of ISOPN. Did the authors see any evidence of that? How would change their results?

Response:

The good agreement of ISOPN between observation and model outputs is obtained by picking the best fit out of a series of sensitivity runs (Figure 5). The original sensitivity analysis results were shown in Figure S8 in the supplement material. We have merged Figure S8 to Figure 5 in the main text, and expanded the discussion on this per the suggestion of the other referee. The ISOPN concentration show very large variations depending on the ISOPN yield (6 to 9%) and NO_x fluxes (5 to 30 pptv m s⁻¹).

For observations, 4,3- ISOPN and 1,4- ISOPN (a mixture of trans- and cis-1,4- ISOPN) were used to calibrate the CIMS. A diurnal average of the changing ISOPN isomer distribution (Fig. S9, obtained from Xiong et al., 2015) was estimated and applied to calibrate ISOPN data for each individual day.

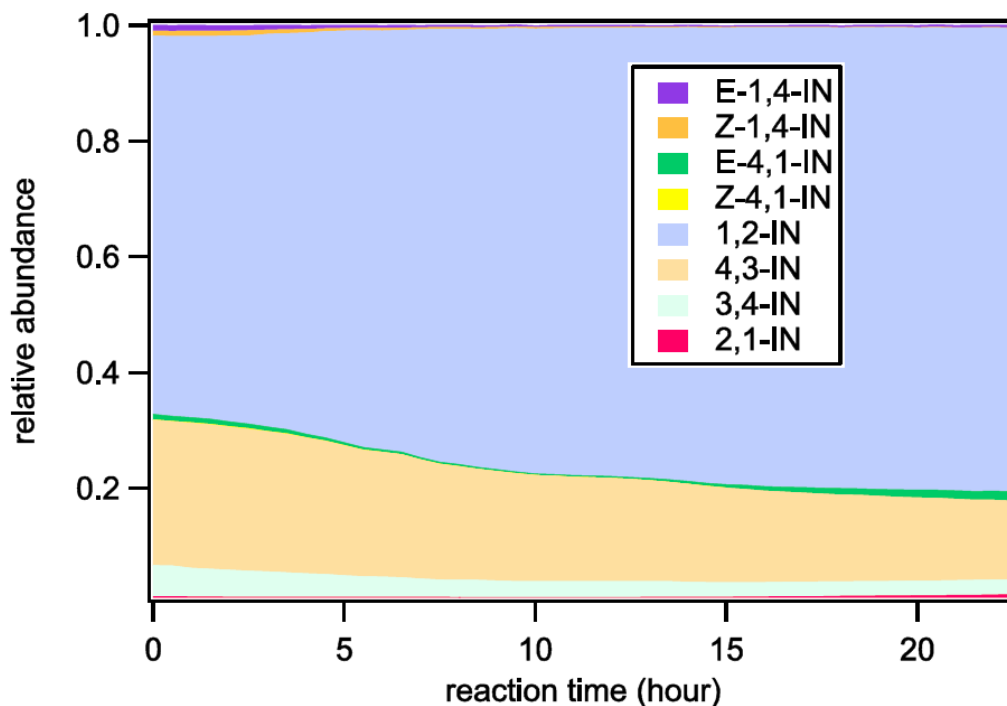


Figure S9. Simulated diurnal IN isomer distribution during SOAS.

For model, applying updated ozonolysis rate for δ -ISOPN ($2.8 \times 10^{-17} \text{ cm}^{-3} \text{ molec.}^{-1} \text{ s}^{-1}$) and β -ISOPN ($3.8 \times 10^{-19} \text{ cm}^{-3} \text{ molec.}^{-1} \text{ s}^{-1}$) (Lee et al., 2014) will cause the model to overestimate ISOPN concentration by 27-56% during 12:00-16:00 CST with $\text{Yield}_{\text{ISOPN}}=6\%$ and $F_{\text{NOx}}=30 \text{ pptv m s}^{-1}$. Aerosol-gas phase chemistry is not implemented in MXLCH, thus we are unable to quantify the influence of hydrolysis on ISOPN. Since ISOPN hydrolysis removes NO_x from the CBL, we would expect a decrease of NO_x concentration if this process was implemented.

Changes:

Line 516-519. The discussions above are added to the main text.

3. It seems to me that comparison of HCHO should be included in Figure 5, if possible. Also I don't see observed HO₂ in Figure 5. It would make sense to make sure that modeled HO₂ is in the right range, before the discussion of NO:HO₂ in the following sections.

Response:

We added HCHO data to the discussion.

HO₂ measurements during our selected study time period are not available due to instrument interference. HO₂ concentration measured on 2013-06-25 (with similar meteorological conditions as the selected days) is $\sim 1.0 \times 10^9$ molec. cm⁻³. The HO₂ concentration from the MXLCH complex scheme is $\sim 7.0 \times 10^8$ molec. cm⁻³ during the same time period, which is 30% less than the observation.

Changes:

Line 480-481. We added the HO₂ comparison to the main text.

4. In Equation 1, what is the role of advection here? Given the lifetime of ozone, I would expect advection plays a role in its budget. This should be discussed and quantified in the text.

Response:

Advection is not implemented for chemical species in MXLCH. This may be added in future versions to account for the impact from advection process.

Changes:

None.

Minor comments:

1. Page 31624 Line 11: "Six isomeric hydroxyl-substituted isoprene peroxy radicals (HOC₅H₈OO; ISOPOO) are then produced." There are minor channels that not considered in current mechanisms. I wouldn't use six here.

Response:

Line 33. We updated the number of pathways to eight according to Orlando et al., 2012.

2. "model outputs generally agree with observations of OH concentration during noontime (Shirley et al., 2006; Hofzumahaus et al., 2009)." Please read the cited papers and check your statement.

Response:

We changed the text to "model outputs generally agree with observations of OH concentration during noontime (Shirley et al., 2006)."

3. Page 31641, Line 4: "The ISOPN yield in the complex scheme is set at 6 %, which is within the range of the results from the chamber experiments (93%) carried out at the SEARCH site (Xiong et al., 2015)." But it appears that the authors use 12% in Table S3. Please clarify this.

Response:

Thanks for pointing this one out. As suggested by the other referee, we decide to expand the discussion on the sensitivity analysis under different ISOPN yields in the main text. Thus we decide to keep the 12% ISOPN yield in Table S3. We added a note in Table S3 to indicate that the stoichiometric coefficient in the reaction equation is for 12% ISOPN yield.

4. Figure 7, it should be "CH₃C(O)OO" not "CH₃(O)OO".

Response:

Thanks a lot for pointing this one out. We corrected this in the main text and Figure legend.

5. Page 31645, Line 4, "One possible explanation of the large discrepancy between model output and observation is the partitioning of ISOP₂OOH to aerosol phase due to its lower vapour pressure and potentially high condensed phase reactivity (Rivera-Rios et al., 2014)." It seems very unlikely that this discrepancy is due to the partitioning.

Response:

Line 631-632. We revised this in the main text.

References

Lance Lee, Alex P. Teng, Paul O. Wennberg, John D. Crouse, and Ronald C. Cohen: On Rates and Mechanisms of OH and O₃ Reactions with Isoprene-Derived Hydroxy Nitrates, *The Journal of Physical Chemistry A* 2014 118 (9), 1622-1637, DOI: 10.1021/jp4107603

Orlando, J. J., and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chemical Society Reviews*, 41, 6294-6317, 2012.

Xiong, F., McAvey, K. M., Pratt, K. A., Groff, C. J., Hostetler, M. A., Lipton, M. A., Starn, T. K., Seeley, J. V., Bertman, S. B., Teng, A. P., Crouse, J. D., Nguyen, T. B., Wennberg, P. O., Misztal, P. K., Goldstein, A. H., Guenther, A. B., Koss, A. R., Olson, K. F., de Gouw, J. A., Baumann, K., Edgerton, E. S., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., and Shepson, P. B.: Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NO_x, *Atmos. Chem. Phys.*, 15, 11257-11272, doi:10.5194/acp-15-11257-2015, 2015.