

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<sub>x</sub>, 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., O<sub>3</sub>), aircraft observations are within the uncertainty range of ground-based observation (Figure 5a). For species with shorter chemical lifetime (e.g., NO<sub>x</sub>, HO<sub>x</sub>), 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 NO<sub>2</sub> (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<sub>x</sub> fluxes (5 to 30 pptv m s<sup>-1</sup>).

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.

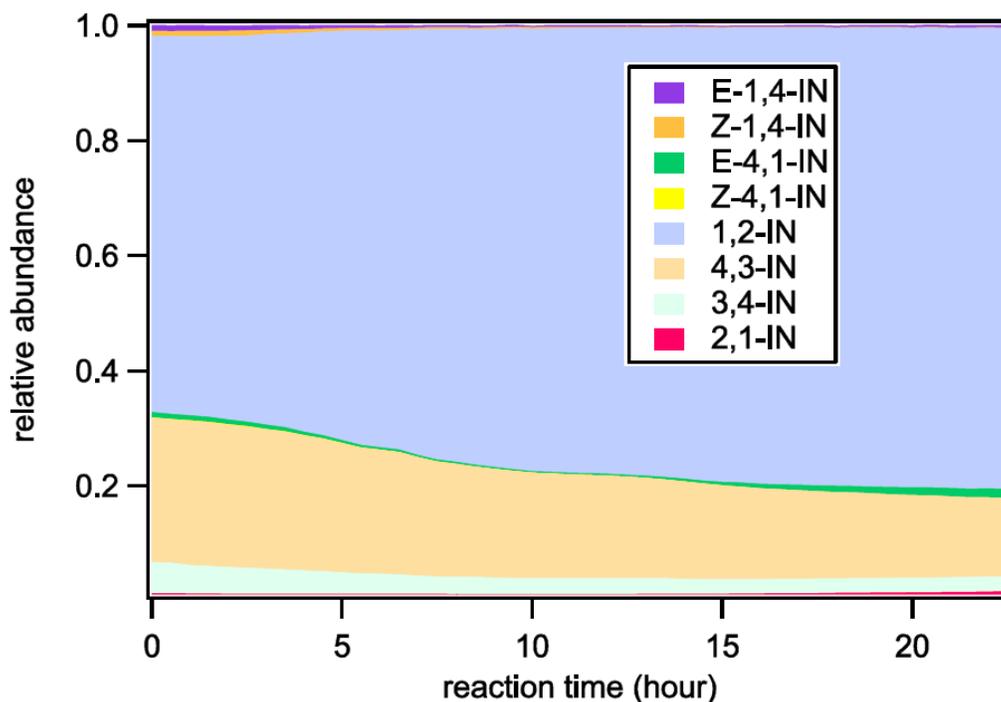


Figure S9. Simulated diurnal IN isomer distribution during SOAS.

For model, applying updated ozonolysis rate for  $\delta$ -ISOPN ( $2.8 \times 10^{-17} \text{ cm}^{-3} \text{ molec.}^{-1} \text{ s}^{-1}$ ) and  $\beta$ -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 NOx from the CBL, we would expect a decrease of NOx 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  $\sim 1.0 \times 10^9 \text{ molec. cm}^{-3}$ . The HO2 concentration from the MXLCH complex scheme is  $\sim 7.0 \times 10^8 \text{ molec. cm}^{-3}$  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 (HOC<sub>5</sub>H<sub>8</sub>OO; 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 "CH<sub>3</sub>C(O)OO" not "CH<sub>3</sub>(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 ISOPOOH 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 O<sub>3</sub> 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<sub>x</sub>, *Atmos. Chem. Phys.*, 15, 11257-11272, doi:10.5194/acp-15-11257-2015, 2015.