We would like to thank the reviewers for their efforts in reviewing this manuscript, and we feel that the manuscript is much stronger with the suggested changes. Below are detailed responses to their comments, which are highlighted in italics.

Reviewer #1

This study focuses on the analysis of the OH and HO2* radicals concentrations and total OH reactivity during the IRRONIC field campaign. The campaign was performed in a forested area characterized by high isoprene emissions and low NO concentrations. Measured radicals, which include a possibly interference-free OH radical measurement, are compared with two mechanisms (RACM2 and MCM) both with and without isomerization reactions for isoprene-RO2 as described within the LIM1 mechanism.

The paper is well written and the data are adequately presented. Though, the analysis of the results and the discussion of the findings is too limited and in the current status this reviewer is not sure it is enough for publication on ACP. Following are some general comments which could help improving the discussion.

One of the problems of this study is the lack of NO data for a large fraction of the campaign. The authors overcome the issue by using the measured diurnal average when no NO data is available. I do not think this is a very good approach. Indeed, a much better solution is to constrain the model to the ozone and NO2 concentrations and jNO2 values and let the model calculate the NO. This is shown only for one model run (MCM 331) but should be done for all the models. Also, the modeled NO concentration should be compared with the measured one to see how well the model is able to reproduce it. This would allow for a better confidence in the models output also for days were no NO measurements are available.

We agree that constraining the model to the measured ozone, NO2, and jNO2 and allowing the model to calculate NO is an alternative approach to addressing the lack of NO measurements in this study. However, the measurements suggest that deviations from the ozone photostationary state were significant at this site, implying that the concentrations of peroxy radicals were high enough to significantly impact the concentration of NO. In addition, the location of the site relatively close to NO sources from transportation as well as soil emissions may also impact the NO/NO2 ratio, as pointed out by Reviewer #2. For these reasons, we chose to constrain the model to the measured diurnal averaged NO to predict the radical concentrations rather than allowing the model to calculate the NO. We have clarified this in the revised manuscript on page 9:

“Zero-dimensional models cannot explicitly account for emissions, and NO is emitted both by vehicles on the nearby highway 1 km to the Southwest and by soil. Such local perturbations to the NOx-O3-radical chemistry necessitate using constrained measurements of NO, NO2, and O3."

However, we have included additional model runs with NO calculated by the model as suggested by the reviewer. Figure 6 in the revised manuscript now includes results from the MCM 3.2 *model in addition to the MCM3.3.1 results. For clarity, the NO unconstrained RACM2 and RACM2-LIM1 results are included in an additional plot in the Supporting Information.*

On days when NO was measured, the modeled calculated NO overpredicted the measured NO during the day, and underpredicted it in the morning and at night, suggesting that the assumption of an NO/NO2 steady-state may not be justified. An additional plot illustrating the inability of the model to reproduce the measured NO is also included in the Supporting Information.

We have added the following to the revised manuscript addressing these points on page 12:

"However, the assumption that NO is in steady-state may not be justified given the location of the site near NO sources from transportation as well as the potential influence of soil emissions (Molina-Herrera et al., 2017). In addition, the measurements suggest that deviations from the ozone photostationary state were significant at this site, implying that the concentrations of peroxy radicals were high enough to significantly impact the concentration of NO. On the days when NO was measured, the models overpredicted the NO measurements by a factor of approximately 2-4 during the day, and underpredicted the measurements in the morning and evening (Fig. S3). This underprediction of the measured NO in the morning and evening may reflect active NO sources from soil and transportation emissions, and could explain why the NO unconstrained model underpredicts the concentration of OH in the afternoon."

It would be good to focus on the days when the measurements are complete and try and understand why there is still a discrepancy between modeled and measured OH radicals even after the inclusion of the LIM1 mechanisms. On those days it could be good to perform an experimental budget if possible. I can understand it could be difficult as the HO2* radical measurement is affected by an interference from RO2 radicals but a % of this interference is given based on laboratory studies so it should be possible to remove it. This would allow for an additional way to assess whether there is a discrepancy between the included sources of OH radicals and the total OH radical production.

Unfortunately there were only a few days during the campaign when the measurements were complete. As discussed in the manuscript, the models including the LIM1 are in better agreement with the measured OH and HO2 concentrations on these days, illustrating the ability of the model to reproduce the measurements when NO was measured simultaneously. For 20 July, the RACM2-LIM1 and MCM 3.3.1 models predict a maximum concentration of OH that are within 30% of the measured concentration, in better agreement than the models without the LIM1 mechanism. We have clarified this in the revised manuscript on page 12 and included an additional figure in the Supporting Information highlighting the agreement of the LIM1 models with the measurements on this day:*

"For the days at the end of the campaign where there was significant overlap between the measurements of OH and NO, the model results are in better agreement during these days (20

and 24 July) (Fig. 5). On 20 July, the RACM2-LIM1 and MCM 3.3.1 models predict maximum OH concentrations that are within 30% of the measured OH on 20 July (Fig. S1).

As pointed out by the reviewer, an experimental budget for the days where the measurements are complete can provide some information regarding the source of discrepancies with the model. An experimental OH radical budget analysis for 20 July suggests that the measured OH production is less than total OH loss. However, including the modeled OH production from the LIM1 mechanism brings the total OH production into reasonable agreement with total OH loss on this day, with the measured OH production rates (including the modeled LIM1 contribution) within 30% of the measured OH loss rate, consistent with the ability of the LIM1 mechanisms to reproduce the maximum measured OH concentration on this day. This is discussed in the revised manuscript on page 15 and the experimental budget is included in the Supporting Material:

"An experimental radical budget for 20 July when the measurements were complete suggests that the total measured OH production rate is nearly balanced by the total OH loss rate calculated by the concentration of individual sinks and the loss rate based on the measured total OH reactivity to within approximately 30% (Fig. S8), consistent with the agreement between the measured and modeled OH on this day as discussed above. For simplicity, the measured HO2 was used to calculate the rate of OH production from the HO2 + NO reaction and as a result the measured production rate represents an upper limit to the overall OH production rate. Thus, the difference between production and loss may be greater than illustrated in this figure, but is still likely to be within the combined uncertainties of all the measurements (for example 38% (2σ) for OH and for HO2), similar to that observed previously (Tan et al., 2019)."*

Both RACM2 and MCM mechanisms are used in this study but there is no discussion about why both are used and, based on the results, which one is able to better reproduce the measured data and why. As both are used extensively within the community a better analysis of the differences between the two should be given. Also, both are implemented with the LIM1 mechanism. Is this done in the same way or are there differences? What is the reason behind the large differences in the modeled HO2* concentrations between the two mechanisms?

As indicated by the reviewer, we chose to use both RACM and MCM mechanisms to model these results given that both are used extensively within the community. While the MCM mechanism is a more explicit mechanism expected to better reproduce complex systems, the lumped RACM mechanism provides a simpler radical budget analysis. We have clarified the reason for using these mechanisms on page 9 of the revised manuscript, in addition to clarifying how the LIM1 mechanism is incorporated in each:

"While the MCM model provides a near-explicit chemical mechanism and is expected to better represent complex chemical atmospheres, the lumped RACM mechanism is easier to use in radical budget calculations. The isoprene oxidation mechanism in RACM2 was updated as described in Tan et al. (2017) to include the Leuven Isoprene Mechanism (LIM1) originally proposed by Peeters, et al. (2009) involving peroxy radical isomerization reactions leading to additional HOx radical production, and includes the LIM1 updated bulk RO2 reactions

described in Peeters et al. (2014). The addition also includes a revision of the chemistry of first-generation isoprene oxidation products, including methyl vinyl ketone (MVK), methacrolein (MACR), and isoprene hydroperoxides (ISHP) (Tan et al., 2017). In addition, the ambient measurements were also modeled with version 3.3.1 of the Master Chemical Mechanism (MCM). In comparison to MCM 3.2, MCM 3.3.1 includes an updated isoprene oxidation mechanism based on the LIM1 mechanism resulting in HOx recycling from peroxy radical H-shift isomerization reactions (Jenkin et al., 2015)."

During an analysis in response to the reviewer noting the difference between the modeled HO2 by the two mechanisms, we found a discrepancy in the model results illustrated in Figure 6. Correcting this discrepancy resulted in better agreement in the modeled HO2*concentrations by the two mechanisms, with predicted maximum concentrations agreeing to within 10%. This has been clarified in the revised manuscript and the corresponding figures and discussion has been updated.*

The total OH reactivity measurement shows that, overall, when the contribution from modelled OVOCs is included, the budget is closed. Though, this is not true for some days when still a certain fraction of OH reactivity is unexplained. It would be good to look if there were differences between these days and the ones were the OH reactivity could be explained…different wind directions, different VOCs distribution, different meteorological conditions, etc. Does this missing reactivity correlate with the days where the measured OH concentration is larger than the modelled one?

We have done an extensive analysis of the missing reactivity measured during this campaign, including analyzing different wind directions, velocity, trajectories, meteorological conditions, etc. and have yet to find an explanation for the missing reactivity. We are continuing this analysis and plan to do additional measurements in the future. This has been clarified on page 15 of the revised manuscript:

"The reason for this discrepancy is unclear, as the missing reactivity on this day did not appear to correlate with changes in wind speed, direction, trajectory, or meteorological conditions, but may indicate the presence of additional unmeasured emissions or oxidation products not accounted for by the model. Additional measurements and analyses will be necessary to determine the source of the missing reactivity."

In general, often it is written the agreement is good or there is better agreement… but there is no value reported of a ratio of model to measurement or correlation coefficient so it is not possible to really assess the correctness of these statements.

We have attempted to include more quantifiable comparisons in the revised manuscript as suggested.

Specific comments:

Abstract: It would be good to have, in addition to percentages, also the mean concentrations of radicals and OH reactivity and what low NOx means.

These suggestions have been added to the abstract.

Page 2, Line 12 to 17. No mention of the recent campaigns performed in China (Tan et al., 2017; Tan et al., 2018; Tan et al., 2019).

We have added these references as suggested.

Page 5, Line 11. Is it pure NO injected to convert HO2 to OH radicals? Or why is the interference from RO2 radicals so large? Would not it make sense to reduce the NO further to reduce the interference?

One of the goals of this study was an instrumental intercomparison of peroxy radical measurements by the IU-FAGE instrument with the HO2+RO2 measurements by the Drexel University Ethane – Nitric Oxide Chemical Amplifier (ECHAMP) instrument. In order to provide a useful intercomparison, high concentrations of NO (10% in N2) were deliberately added to the IU-FAGE instrument to allow for efficient conversion of isoprene peroxy radicals in addition to HO2. Given that the total peroxy radical concentrations at this site were primarily HO2 and isoprene peroxy radicals, the resulting HO2 measurements were found to be similar to the total HO2+RO2 measurements by the ECHAMP instrument. The results of this intercomparison are summarized in a separate publication (Kundu et al., 2019). This has been clarified on page 7 of the revised manuscript:*

"A high concentration of NO leading to a high conversion efficiency of isoprene-based peroxy radicals to HO2 was used throughout the study to provide a useful intercomparison of the IU-FAGE HO2 measurements with the RO2+HO2 measurements by the Drexel University Ethane – Nitric Oxide Chemical Amplifier (ECHAMP) instrument (Kundu et al., 2019), as HO2 and isoprene-based peroxy radicals accounted for approximately 70% of the total peroxy radicals at this site (see below)."*

Page 9, Line 1. Is the LIM or the LIM1 included in both RACM2 and MCM 3.3.1?

The updated RACM2 mechanism (RACM2-LIM1) described in Tan et al. (2017) includes updates to the LIM rates as described in Peeters et al., 2014. This has been clarified in the revised manuscript. The MCM 3.3.1 mechanism also includes the updated LIM1 mechanism as described in Jenkin et al., (2015) and this has been clarified in the revised manuscript, as noted above.

Page 10, Line 34. What does it mean that measurements on the 21-22 July focused on the HO2* thus OH measurements were not available? The instrument should measure OH and HO2 radicals in parallel or? How is stopping the OH measurement going to improve the measurement of HO2* radicals?

The IU-FAGE instrument is composed of a single detection axis for measuring both OH and HO2, and as a result cannot measure OH and HO2 simultaneously. This has been clarified on page 4 of the revised manuscript:

"The Indiana University LIF-FAGE instrument (IU-FAGE) has been described in detail previously and consists of a single axis for alternating measurements of OH and HO2 or HO2 (Dusanter et al., 2009a Griffith et al., 2013; 2016)."*

For most of the campaign, NO was added for 30 seconds every 30 minutes to measure HO2, while OH was measured during the remaining time. As part of the peroxy radical intercomparison with the Drexel University ECHAMP instrument, NO was added continuously on 21-22 July to allow for higher time resolved measurements of HO2*. Because NO was added continuously during this time, no OH measurements were made on these days. This has been clarified on page 11 of the revised manuscript:*

"Measurements on 21-22 July focused on measurements of HO2 as part of the peroxy radical informal instrumental intercomparison (Kundu et al., 2019), with NO added continuously to the detection cell to provide measurements with a higher time resolution. Thus OH measurements were not conducted on these days."*

Page 16, Line 9. What does "similar OH" stands for?

This has been revised to "similar concentrations of OH have been observed at this site…"

Figure 5. Colors of the models are different between OH and HO2* panels.

We have corrected the panels so that the color of the model results are consistent.

Figure 12. Suggest to have consistency of the colors within the upper and lower panels.

We have revised the colors as suggested.