Dear Dr. Hofzumahaus,

Thank you for your review of our revised manuscript and the return of the reviewer's comments. We have revised the manuscript as you and the reviewers have suggested, and feel that the manuscript is much improved. Below are our responses to yours and the reviewer's comments, highlighted in italics, with changes to the manuscript highlighted in red.

Editor's Comments

The revised paper has been reviewed again by two referees. Referee #1 proposes to reject the paper mainly because of insufficient availability and quality of data, while Referee #3 recommends publication with minor revisions. The requested revisions, however, are substantial and concern the lack of NO data needed for the interpretation of the radical chemistry.

I think that both referees make some good points. I share the view of Referee #3 that the paper contains valuable information that is worth to be published. It is of general interest that a significant OH interference of roughly a factor of 2 has been observed in the Indiana University LIF-FAGE instrument in a forest environment by using a chemical modulation technique. This information is relevant because similar types of instruments have reported in the past unexplained high OH concentrations in environments with high isoprene and low NO concentrations. The present work also demonstrates the usefulness of the chemical modulation method that was introduced by Mao et al. (2012). Furthermore, the well characterized data set for HO2*, which is essentially the sum of HO2 and isoprene peroxy radicals, and the measured OH reactivities are also of interest in combination with interference-corrected OH data.

I share the view of Referee #1 and #3 that the use of a mean diurnal NO profile for the intepretation of the complete radical data set is problematic. There are large gaps in the measured time series of OH and NO, which show little temporal overlap between the records. The paper presents all arguments why it is not reasonable to use the averaged diurnal NO profile for OH model calculations which are then compared to the measured OH. First, NOx levels were much higher in the first period of the campaign, when most of the OH data were measured, compared to the second period, when most NO data were recorded. Second, missing NO could not be calculated from the available NO2 measurements, because the photostationary state was strongly perturbed by local NO sources. In such an environment, the lack of measured NO data prevents firm conclusions from comparisons between modelled and measured OH, as the production of OH is dominated by the reaction of HO2+NO. Following the recommendation of Referee #3 and in agreement with comments by Referee #1, I suggest that the authors revise their paper and restrict the model interpretation of OH and HO2* only to those periods when NO and NO2 are simultaneously available. Though this means that only a few days can be used for comparison between model and measurements, the conclusions are expected to be significantly more robust than in the current paper version. This may provide better constraints to answer the important question, whether we are still lacking unknown OH (or HO2) radical sources in current atmospheric chemical mechanisms. When your revise the manuscript, the suggestions by the referees should be taken into account. In addition, I also have a few specific suggestions that should be considered.

As recommended, we have revised the paper and focused the discussion of the model interpretation to the few days where both OH and NO were available. The diurnal average of this data with the model results has been included as a new figure in the revised manuscript. We have removed the model results for days when NO measurements were not available, and removed the discussion of the model results with NO unconstrained. The discussion of the model results is now focused on these days, and the relevant figures *have been updated. While the main conclusions of the paper have not changed, we have added the a discussion of the results of this new analysis to the paper.*

Editor's suggestions

- The magnitude of the measured OH interference should be mentioned in the abstract.

We have included the magnitude of the average interference in the abstract as suggested.

"Using an OH chemical scavenger technique, the study revealed the presence of an interference with the LIF-FAGE measurements of OH that increased with both ambient concentrations of ozone and temperature, with an average daytime maximum equivalent OH concentration of approximately 5×10^{6} cm^{-3}."

- The quoted literature on the chemistry of isoprene is not up-to-date. Since the LIM1 mechanism was published by Peeters et al. (2014), there have been new studies presented by Peeters (2015), Teng et al. (2017), Wennberg (2018), Berndt et al. (2019), Müller et al. (2019) and Novelli et al. (2020). For references and review of the differences in the mechanisms, see the recent paper by Novelli et al. (2020). It should be noted that the LIM1 mechanism and the isoprene mechanism in MCM v3.3.1, which are both used in the present study, are not the same, as they use different rate coefficients for the LIM1 chemistry. This should be clarified on page 9, line 12-13.

We have expanded the discussion of isoprene chemistry, updating the references as suggested. We have also clarified the differences in the rate coefficients for the bulk isomerization rate constants between the LIM1 mechanism and MCM 3.3.1 on page 9 of the revised manuscript as suggested.

"The bulk peroxy radical isomerization rate constants in MCM 3.3.1 are based on the recommendations of Peeters (2015), which are approximately a factor of 5 lower than the original LIM1 recommended rates (Peeters, 2015; Novelli et al., 2020) in order to bring the model predictions into better agreement with experimental measurements of the production of HPALDs and other products (Crounse et al., 2011; Teng et al., 2017; Wennberg et al., 2018; Berndt et al., 2019)."

- Page 5, line 7. Does the laser power (0.5 - 4.4 mW) apply to a single laser beam, or to overlapping laser beams?

We have clarified that this laser power reflects the power entering the sampling cell and does not represent the power density due to overlapping beams inside the detection cell on page 5 of the revised manuscript.

"For this campaign, the laser power entering the sampling cell ranged from 0.5 to 4.4 mW and was monitored using a photodiode at the exit of the White cell. This does not reflect the laser power density inside the detection cell due to overlap of the beams in the multipass configuration."

- In Figure 5, a considerable number of interference-corrected OH data points have negative values that are more than 3sigma less than zero. Why? Is it possible that the chemical modulation is overcorrecting the interference or is the precision of the OH data worse than indicated by the error bars? This point is also addressed by Referee #1 who is wondering about the negative OH concentration in the afternoon of July 20 (Figure S1). In Figure S8, this data has apparently been discarded and replaced by estimated values. The figure caption only mentions "Concentrations of OH in the afternoon were estimated due to the poor precision of the data." Please explain the reason and how the estimate was done.

The large negative values (which occurred primarily at night) reflect the fact that the interference was not measured simultaneously as the OH measurements. Because the interference during these times was much larger than the ambient OH signal, large variations in the interference between measurement cycles often resulted in additional scattering in the net ambient OH signals derived from subtraction of the interference, which sometimes exceeded the precision of individual measurements (OH plus interference and the interference). This has been clarified on page 11 of the revised manuscript.

"Because the interference was not measured simultaneously as the ambient OH measurements, subtraction of the measured interference often resulted in both apparent negative concentrations as well as large positive concentrations at night. These large positive and negative values reflect the fact that the nighttime measurements of the interference was much greater than the ambient OH signals and was highly variable between measurement cycles (Fig. 3), resulting in an ambient OH measurement uncertainty that was sometimes larger than the precision calculated from a quadratic propagation of the errors associated with the individual measurements of the ambient OH plus the interference and the interference alone."

The experimental radical budget in the supplement (formally Figure S8) has been revised to include an average of all days that include NO measurements, and with the additional data, estimation of missing OH concentrations for this particular day is no longer necessary.

- When the measured OH concentrations from the IRRONIC campaign are compared with different models, I recommend to compare the outcome with the results derived by Novelli et al. (2020) from chamber experiments. She investigated the photooxidation of isoprene by OH in synthetic air at ambient conditions and comparable low NO concentrations. The measured OH is compared with predictions by different chemical mechanisms including MCM v3.3.1 (Figure 5, 6) and LIM1 (Figure S5), which are also used in the present work.

As suggested, we have included a comparison of the results presented here with the results of Novelli et al. (2020), who also compared their measurements in the SAPHIR chamber and found that the MCM 3.3.1 mechanism underpredicted the OH measurements. They found that a model incorporating bulk isoprene peroxy radical isomerization rates similar to that used in the LIM1 mechanism were in better agreement with the measurements, similar to that reported here. This discussion has been added to page 12 of the revised manuscript as well as in the Summary.

"Including versions of the LIM1 mechanism for HOx regeneration in both the MCM (3.3.1) and RACM2 (RACM2-LIM1) models result in higher modeled daytime concentrations of OH compared to the base MCM 3.2 and RACM2 mechanisms, with the RACM2-LIM1 results in better agreement and within 30% of the measured concentrations during the day (9:00-17:00 EDT) (Fig. 5), while the MCM 3.3.1 model underpredicted the measurements during this period by approximately a factor of 2. These results are similar to that found by Novelli et al. (2020), who found that the MCM 3.3.1 underpredicted measurements of OH by a factor of approximately 1.4 during isoprene oxidation experiments in the SAPHIR chamber. The measured OH concentrations could be reproduced using a model that increased the yield of HPALD in the oxidation mechanism, resulting in an effective bulk isoprene peroxy radical isomerization rate similar to that in the original LIM1 mechanism (Novelli et al., 2020). These larger bulk peroxy radical isomerization rates are incorporated into the RACM2-LIM1 mechanism used in the present study (Tan et al., 2017), leading to the higher modeled radical concentrations compared to the RACM2 and MCM model results shown in Fig. 5."

- Figure S8. I agree with Referee #1. Since HO2* contains a well characterized fraction of isoprene peroxy radicals, I suggest to use interference-corrected HO2 concentrations for the OH budget analysis.

While the contribution of isoprene peroxy radicals to HO2 has been quantified in the lab, correcting the ambient measurements for the interference requires a knowledge of the ambient concentration of isoprene peroxy radicals, which for this study can only come from model predictions. For the experimental radical budget shown in the supplement, we chose to use the experimentally measured HO2* concentrations rather than corrected HO2 concentrations based on model predictions. However, for this revision we have included the estimated contribution of the HO2+NO reaction to the experimental OH radical budget based on estimates of the ambient HO2 concentration from the measured HO2* concentrations and the modeled HO2/HO2* ratio.*

- Is there any explanation for the relative high midnight isoprene values (1ppbv)? For comparison, Tan et al. (JGR, 2001) report 10 times lower nocturnal isoprene concentrations in an isoprene emitting forest in summer 1998.

The high nighttime mixing ratios of isoprene observed at this site are likely due to the fact that the measurements were conducted near the surface and below the forest canopy, in contrast to the measurements by Tan et al. (2001) which were sampled approximately 10-m above the forest canopy on top of the 31-m PROPHET tower. Because the measurements in this study were conducted below the forest canopy, vertical stratification likely resulted in higher concentrations of isoprene trapped near the surface during several nights. This has been clarified on page 10 of the revised manuscript.

"The relatively high nighttime mixing ratios often observed at this site are likely due to the fact that the measurements were made below the forest canopy and relatively close to the surface. As a result, vertical stratification likely resulted in higher concentrations of isoprene near the surface during several nights, similar to other measurements of biogenic VOCs below the forest canopy (Bsaibes, et al., 2020)."

- The paper uses EDT time. When was local noon?

Local solar noon at this site occurred at approximately 13:52 EDT. This has been clarified on page 4 of the revised manuscript.

- Page 17, line 25: Typo. It must read "Rohrer".

This typo has been corrected.

- Table 1. Add footnote explaining HO2*.

We have added a footnote defining HO2 to the table, as suggested.*

Reviewer 2

I have reviewed the manuscript in view of the interactive public discussion, looking at the reports of the reviewers, the responses and the revised MS and supplement. I am happy that the authors have in general responded satisfactorily to the reviews, and made appropriate changes to the MS. There are a few areas though where some further clarifications are needed.

The lack of NO measurements during the campaign, and the probable local sources of NOx (soil, traffic) causing the stated deviation from steady-state (also from large concentrations of peroxy radicals), means that alternate methods of estimating NO during these periods, e.g. from NO2 measurements, seemingly are not easy to implement. This is clearly stated in the paper. Therefore focussing on the periods were both NO and NO2 measurements are available is sensible and being careful that average diel profiles of model calculations and therefore conclusions regarding the level of agreement are only generated from periods where NO data are available to constrain the model. There are NO data though for significant periods, which makes the model comparison a useful and valid thing to do. Figure 1 and Figure S3 certainly supports the idea that NO is not in photostationary state with NO2, and there are local sources (soil, traffic) – which is now clearly stated in the revised MS.

As mentioned above, we have revised the discussion of the model comparison to the days when NO was measured, as suggested.

Page 7 (revised MS) lines 1-6, it is not clear why just HO2* was measured? I realise this means that a comparison with the ethane PERCA instrument (some of HO2+RO2) could be performed (the latter measuring HO2+mainly isoprene RO2 which forms an interference in HO2), and this was the subject of a previous publication, but was the NO ever switched to a low value some of the time to enable HO2 measurements periodically to compare with modelled HO2?

Unfortunately, because a major goal of the campaign was the intercomparison with the ECHAMP instrument, the NO concentration added to the instrument was not reduced during the campaign to measure HO2 for comparison with the model.

The OH interference, although sometimes significant, has been characterised for this instrument, and so there should be confidence that the OH measurements from OHchem are accurate. Also, it is fairly likely that HO2* is the sum of HO2 and some fraction of isoprene peroxy radicals (which is characterised in the lab and with this RO2 being the main RO2 species). From this point of view the measurement time-series of radicals of OH and HO2* is valuable, and as the data have not been over interpreted and sensible comparisons with the model have been made (i.e. where NO measurements are available to constrain the model), then this is a worthwhile contribution.

Some subjective phrases have been made more quantitative. Please check this has been done for all phrases like “good” and “better” are made more quantitative.

We have attempted to provide more quantitative statements throughout the manuscript as suggested.

The correction factor of 1.4 for the OH reactivity is interesting (and determined from lab studies of known sinks) – was this seen in the intercomparison also during the ambient measurements?

The correction factor was determined from additional laboratory studies before and after the peroxy radical intercomparison, and was consistent with the laboratory measurements described in Hansen et al. (2014). This has been clarified on page 9 of the revised manuscript.

“Laboratory measurements of the reactivity of several VOCs with well-known rate constants, including butane, isoprene, and propane showed that the OH reactivity measurements for these compounds were on average 30% lower than calculated when the measured velocity of the turbulent core is used to determine the reaction time. This consistent underestimation of the OH reactivity is likely due to either incomplete mixing of the reactants or a systematic underestimation of the reaction time, and is similar to that measured previously by Hansen et al. (2014).”

In response to reviewer 2’s comment regarding P10 L5, it is stated that “the correlation in the present study was not statistically significant”.

Can this be clarified, e.g. in terms of a correlation coefficient r or something similar, otherwise again the statement is a little subjective?

We have added the R2 value for the correlation as suggested and refined the statement on pages 10-11 of the revised manuscript.

“This result is also consistent with the measurements of Novelli et al. (2017), who found that their observed interference correlated with the product of ozone and biogenic VOC concentrations, although the correlation in the present study was weak ($R^2 = 0.15$).”

There is a statement in the conclusions about the level of OH before the interference is subtracted (OHwave going up to around 9x10(6)). There ought to be something similar in the abstract. The abstract has the level of OH stated after interference subtracted (4x10(6)) but it is not possible currently to gauge the level of interference from the abstract, and this is something that ought to be there.

We have added the level of the interference in the abstract as suggested.

“Using an OH chemical scavenger technique, the study revealed the presence of an interference with the LIF-FAGE measurements of OH that increased with both ambient concentrations of ozone and temperature, with an average daytime maximum equivalent OH concentration of approximately 5×10^6 cm^{-3}.”

The following comments use Page – line number (e.g. 2-17) for the revised MS.

4-25. Bottorff et al., 2015; manuscript in preparation?? Do you mean 2020?

We have clarified the citations, with the Bottorff et al., 2015 referring to an earlier AGU presentation, and Bottorff et al., 2020 referring to the manuscript in preparation.

17-9. For the “similar concentrations of OH were observed at this site in 2017...” were these concentrations after interference subtracted - just clarify.

We have clarified that these concentrations were after the interference was subtracted.

Figure S8 left hand side panel - shows a budget calculation of OH production, but uses HO2* rather than HO2 to calculate HO2+NO. Could there be a statement (in the caption or the main text) saying what roughly the HO2*/HO2 ratio and hence what the degree of overestimation is of HO2+NO, as there are already missing sources of OH (comparing to the loss rate OHxk(OH)) even using HO2*+NO.

As discussed above, we have revised this figure using the estimated HO2 concentrations based on the modeled HO2/HO2 ratio. We have indicated the ratio used in the caption to this figure as suggested.*

Reviewer 1

Unfortunately, the revised version is still not satisfactory.

No strong point can be made with the data presented in this paper and therefore there is no advantage of having this study published. The lack of reliable NO data and the inability of the model in reproducing the measured NO when available makes it impossible, in my opinion, to use to data to make any statement on the OH radical production sources and/or missing ones.

We understand the reviewers concerns, and as discussed above we have confined the modeling to the period when NO measurements were available to provide a more meaningful comparison to the measurements. We have also expanded the discussion of potential missing radical sources based on the results of the models which are now fully constrained by the available NO measurements.

Also the quality of the radical measurement is questionable. The newly added figure S1 shows the comparison measurements and model for one day with available NO data. First, what can be really learned from having 2 OH data point in 6 hours (between 6 and 12 UTC)? Second, is really the OH radical concentration negative between 14 and 16? What about the huge discrepancy during the night?

Unfortunately, instrumental problems limited the measurements on the day in question, limiting the number of points for comparing with the model. As discussed above, the large negative values (which occurred primarily at night) reflect the fact that the interference was not measured simultaneously as the OH measurements. Because the interference during these times was much larger than the ambient OH signal, large variations in the interference between measurement cycles often resulted in additional scattering in the ambient OH concentration that was sometimes outside the precision of individual measurements (OH plus interference and the interference)

To provide a more robust comparison with the model, we compared the diurnal average of the measurements during the period with NO measurements. The early evening and nighttime measurements during this period are similar to that observed during the entire campaign, and are also similar to measurements made at this site by the IU-FAGE instrument and the University of Colorado CIMS instrument in 2017 as part of an informal instrument intercomparison. The discrepancy between the nighttime measurements and the model suggest that there may be a missing radical source in the model, although additional measurements will be needed to resolve this discrepancy. An expanded discussion regarding the model-measurement agreement has been added on page 12 of the revised manuscript.

"Including versions of the LIM1 mechanism for HOx regeneration in both the MCM (3.3.1) and RACM2 (RACM2-LIM1) models result in higher modeled daytime concentrations of OH compared to the base MCM 3.2 and RACM2 mechanisms, with the RACM2-LIM1 results in better agreement and within 30% of the measured concentrations during the day (9:00-17:00 EDT) (Fig. 5), while the MCM 3.3.1 model underpredicted the measurements during this period by approximately a factor of 2. These results are similar to that found by Novelli et al. (2020), who found that the MCM 3.3.1 underpredicted measurements of OH by a factor of approximately 1.4 during isoprene oxidation experiments in the SAPHIR chamber. The measured OH concentrations could be reproduced using a model that increased the yield of HPALD in the oxidation mechanism, resulting in an effective bulk isoprene peroxy radical isomerization rate similar to that in the original LIM1 mechanism (Novelli et al., 2020). These larger bulk peroxy radical isomerization rates are incorporated into the RACM2-LIM1 mechanism used in the present study (Tan et al., 2017), leading to the higher modeled radical concentrations compared to the RACM2 and MCM model results shown in Fig. 5."

"Although the RACM2-LIM1 mechanism appears to be able to reproduce the daytime OH radical measurements compared to the MCM 3.3.1 mechanism, all the models underestimate the measurements in the early evening and night. While there is uncertainty associated with these nighttime measurements due to the large interference that was subtracted, similar concentrations of OH were observed during the evening by both the IU-FAGE instrument and the University of Colorado Chemical Ionization Mass Spectrometry (CIMS) instrument at this site in 2017 during an informal instrument intercomparison (Rosales et al., 2018; Reidy et al., 2018). These results suggest that there may be a missing radical source during this period, such as the ozonolysis of unmeasured biogenic VOCs, and additional measurements will be required to resolve this discrepancy."

It is not justifiable to use the HO2* in the budget plot (Fig. S8) saying it is an upper limit. The authors already argue HO2* is affected by the contribution of isoprene RO2 and they even give number to how much those contribute to the total HO2* signal from the model result. So, that contribution should be taken out and only the HO2 radical should be used in the budget as in this case it is not a small interference but the measurement was done to increase the detection of such radicals.

As discussed above, we chose to use the experimentally measured HO2 concentrations for the experimental radical budget rather than corrected HO2 concentrations based on model predictions. However, for this revision we have estimated the concentration of HO2 based on the modeled HO2/HO2* ratio to determine the contribution of the HO2+NO reaction to the experimental OH radical budget and have included other modeled radical sources for comparison in a revised figure.*

To summarize, the quality of the measurements is not such to justify any findings or answers to scientific questions. Indeed there is no strong statement in the paper which just shows data with a comparison with a model but with no effort in making some analysis of the findings as the data do not allow for such. For that reason, I suggest rejection of the paper as publication in ACP requires for a study to have substantial contribution to scientific (substantial new concepts, ideas, methods, or data).

As mentioned above, we have expanded the discussion of the model-measurement agreement using only the data when all the measurements are available. While this reduces the amount of data, it does provide a more robust analysis of the data, which has been included in the revised manuscript.

OH and HO_2 radical chemistry in a midlatitude forest: Measurements and model comparisons

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Abstract. Reactions of the hydroxyl (OH) and peroxy radicals (HO_2 and RO_2) play a central role in the chemistry of the atmosphere. In addition to controlling the lifetimes of many trace gases important to issues of global climate change, OH radical reactions initiate the oxidation of volatile organic compounds (VOCs) which can lead to the production of ozone and secondary organic aerosols in the atmosphere. Previous measurements of these radicals in forest environments characterized by high mixing ratios of isoprene and low mixing ratios of nitrogen oxides (NO_x) (typically less than 1-2 ppb) have shown serious discrepancies with modeled concentrations. These results bring into question our understanding of the atmospheric chemistry of isoprene and other biogenic VOCs under low NO_x conditions.

During the summer of 2015, OH and HO_2 radical concentrations as well as total OH reactivity were measured using Laser-Induced Fluorescence - Fluorescence Assay by Gas Expansion (LIF-FAGE) techniques as part of the Indiana Radical, Reactivity and Ozone Production Intercomparison (IRRONIC). This campaign took place in a forested area near the Indiana University, Bloomington campus characterized by high mixing ratios of isoprene and low mixing ratios of NO_x. Supporting measurements of photolysis rates, VOCs, NO_x, and other species were used to constrain a zero-dimensional box model based on the Regional Atmospheric Chemistry Mechanism (RACM2) and the Master Chemical Mechanism (MCM). Using an OH chemical scavenger technique, the study revealed the presence of an interference with the LIF-FAGE measurements of OH that increased with both ambient concentrations of ozone and temperature, with an average daytime maximum equivalent OH concentration of approximately 5×10^6 cm^{-3}. Subtraction of the interference resulted in measured OH concentrations of

approximately 4×10^6 cm^{-3} (average daytime maximum) that were in better agreement with model predictions to within approximately 30%, although the models underestimated the measurements in the evening. Measurements of HO_2 concentrations during the campaign (approximately 1×10^9 cm^{-3} average daytime maximum) included a fraction of isoprene-based peroxy radicals ($HO_2*=HO_2 + \alpha RO_2$) and were found to agree with model predictions to within approximately 10-30%. On average, the measured reactivity was consistent with that calculated from measured OH sinks to within 20%, with modeled oxidation products accounting for the missing reactivity, although significant missing reactivity (approximately 40% of the total measured reactivity) was observed on some days.

1 Introduction

The hydroxyl radical (OH) is one of the primary oxidants in the atmosphere (Levy, 1972). The OH radical initiates the oxidation of volatile organic compounds (VOCs) that leads to the production of hydroperoxy radicals (HO_2) and organic peroxy radicals (RO_2). In the presence of nitrogen oxides (NO_x = NO + NO_2), reactions of these radicals can lead to the production of ozone and secondary organic aerosols in the atmosphere, the primary components of photochemical smog. Because of their short atmospheric lifetimes, measurements of OH and HO_2 (together HO_x) and total OH reactivity can provide a robust test of our understanding of this complex chemistry (Heard and Pilling, 2003).

Multiple field campaigns have been conducted over the years measuring OH and HO_2 radicals in both urban and forested environments. Measurements of OH in urban areas characterized by high mixing ratios of NO_x and anthropogenic VOCs have been generally consistent with model predictions (Ren et al., 2003; Shirley et al., 2006; Kanaya et al., 2007a; Dusanter et al., 2009b; Hofzumahaus et al., 2009; Griffith et al., 2016; Tan et al., 2017; 2018; 2019), while measurements in remote forested environments characterized by low mixing ratios of NO_x and high mixing ratios of biogenic VOCs have often been greater than model predictions (Tan et al., 2001; Lelieveld et al., 2008; Whalley et al., 2011; Rohrer et al., 2014).

However, recent measurements by Mao et al. (2012) in a northern California forest using a new chemical scavenging technique that removes ambient OH before air enters the detection cell revealed a significant interference associated with their Laser-Induced Fluorescence (LIF) measurements of OH. The unknown interference was a factor of 2 to 3 times higher than ambient OH concentrations (Mao et al., 2012). Similar results were observed in a boreal forest by Novelli et al. (2014), who observed an interference using a similar chemical scrubbing technique that was a factor of 3 to 4 times higher than ambient OH concentrations. One possible source of this observed interference may be the decomposition of Criegee intermediates produced from the ozonolysis of biogenic emissions in the low-pressure detection cells used by LIF instruments, although the ambient concentration of these intermediates in the atmosphere may be too low to explain all of the observed interference (Novelli et al., 2017; Rickly and Stevens, 2018). Another proposed source of the interference is the decomposition of ROOOH molecules inside the FAGE detection cell formed from the reaction of OH with RO_2 radicals (Fittschen et al., 2019). Nevertheless, interferences associated with measurements of OH could explain part of the discrepancies between measured and modeled OH concentrations in forested environments. Monitoring potential interferences associated with OH measurements using LIF techniques may be crucial for understanding the discrepancies between measurements and models.

In contrast to measurements of OH, the agreement between measured and modeled HO_2 concentrations have been highly variable. In urban environments, measured HO_2 concentrations were sometimes found to agree with model predictions (Shirley et al., 2006; Emmerson et al., 2007; Dusanter et al., 2009b; Michoud et al., 2012; Lu et al., 2013; Ren et al., 2013; Griffith et al., 2016; Tan et al., 2017), while other times the measurements were found to be both lower (George et al., 1999; Konrad et al., 2003) and higher than model predictions (Martinez et al., 2003; Ren et al., 2003; Emmerson et al., 2005; Kanaya et al., 2007a; Chen et al., 2010; Sheehy et al., 2010; Czader et al., 2013; Griffith et al., 2016; Tan et al., 2018). In forested environments, measured HO_2 concentrations were sometimes found to agree with model predictions (Tan, D. et al., 2001; Ren et al., 2005; 2006), but were often found to be either lower (Carslaw et al., 2001; Kanaya et al., 2007b; Whalley et al., 2011; Kanaya et al., 2012; Mao et al., 2012; Griffith et al., 2013; Mallik et al., 2018), or higher than model predictions (Carslaw et al., 2001; Kubistin et al., 2010; Kim et al., 2013; Hens et al., 2014). Part of this variability may be due to interferences from alkene and aromatic based RO_2 radicals converting to HO_2 in systems that detect HO_2 through conversion to OH by addition of NO in the sample cell. The degree to which the RO_2 species can interfere with HO_2 measurements has been quantified through several laboratory experiments (Fuchs et al., 2011; Whalley et al., 2013; Lew et al., 2018) and estimated in some field studies (Hens et al., 2014; Crowley et al., 2018; Mallik et al., 2018). However, the extent of RO_2 radical contributions during HO_2 measurements in many of the campaigns mentioned above is unclear.

Total OH reactivity measurements can complement HO_x measurements by providing a constraint on the total loss of OH that can be compared to that calculated from co-located measurements of OH sinks. Several recent studies have identified discrepancies between measured and calculated OH reactivity in which the measured values are significantly greater than the calculated values (Di Carlo et al., 2004; Hansen et al., 2014; Nölscher et al., 2016; Zannoni et al., 2016; Bsaibes et al., 2020). This difference has been attributed to OH loss from unmeasured VOCs and their oxidation products. In general, significant missing OH reactivity has not been observed as often in urban environments as it has in forested areas, bringing into question our understanding of the chemistry of biogenic emissions and their oxidation products (Dusanter and Stevens, 2017).

This study reports measurements and model simulations of HO_x radical chemistry as well as OH reactivity for a forested site located in Bloomington, Indiana during the 2015 IRRONIC (Indiana Radical Reactivity and Ozone productioN InterComparison) field campaign. This work compares the measured HO_x radical concentrations to model predictions incorporating the Regional Atmospheric Chemistry Mechanism 2 (RACM2), in addition to a version updated to include the Leuven Isoprene Mechanism (RACM2-LIM1), as well as the Master Chemical Mechanism versions 3.2 and 3.3.1 in order to test the ability of each model to reproduce the observed radical concentrations and total OH reactivity.

2 Experimental section

2.1 IRRONIC location and supporting measurements

The IRRONIC campaign site was located within a mixed deciduous forest (sugar maple, sycamore, tulip polar, ash and hickory trees) at the Indiana University Research and Teaching Preserve (IU-RTP) field lab (39.1908º N, 86.502º W) located approximately 2.5 km northeast of the center of the Indiana University campus, and 1 km from the IN 45/46 bypass at the northern perimeter. The goals of the campaign included an informal intercomparison of peroxy radical measurements by two different techniques (Kundu et al., 2019), an analysis of ozone production sensitivity at this site (Sklaveniti et al., 2018), a comparison of measured OH radical reactivity with that calculated from measured VOCs, and a comparison of measured OH, HO_2, and RO_2 radicals with model predictions. The main biogenic emission within this area was isoprene, with an average daytime maximum mixing ratio of approximately 4 ppb during the campaign. This area exhibited low anthropogenic influence from the campus area, with an average daytime maximum mixing ratio of NO of approximately 315 ppt and an average day-time maximum NO_2 mixing ratio of approximately 2 ppb. Measurements were conducted on top of two scaffolding platforms adjacent to the field lab, approximately 1.8 m from the ground. At this site, solar noon occurred at approximately 13:52 EDT. Additional information regarding the field site and the IRRONIC campaign can be found in Sklaveniti et al. (2018) and Kundu et al. (2019).

Table 1 summarizes the major instrumentation employed during the campaign. NO was measured every 10 s using a chemiluminescence instrument (Thermo model 42i-TL, detection limit 50 ppt / 2 min). Periodic problems with the sensor's high voltage power supply that required an eventual replacement limited the coverage of the measurements. NO_2 was measured every 1 s by a Cavity Attenuated Phase Shift (CAPS) instrument (detection limit 40 ppt / 10 s), and ozone was measured every 10 sec using a 2B Technologies model 202 UV absorbance instrument (detection limit 3 ppb / 10 s). Further details on the calibration and baseline measurements for the NO, NO_2, and O_3 measurements are described in Kundu et al. (2019). Nonmethane hydrocarbons, including C2-C10 alkanes and alkenes, butadiene, C6-C9 aromatic compounds, isoprene, α-pinene, and β-pinene, were measured using a thermal desorption GC/FID instrument with a 1.5-h time resolution. Oxygenated VOCs (OVOCs), including C2-C10 aldehydes, C2-C6 ketones, and C2-C4 alcohols, were measured by thermal desorption GC/FID-MS with a 1.5-h time resolution. Offline sampling focused on measurements of oxygenated VOCs including formaldehyde and C2-C6 aldehydes, acetone, MEK, glyoxal and methylglyoxal using DNPH cartridges and HPLC-UV analysis. C6-C16 VOCs including α-pinene, β-pinene, limonene, camphene, heptane-hexadecane, methylpentene-pentadecene were measured using Sorbent cartridges and GC-MS analysis. Measurements of $J(NO_2)$ were made by spectral radiometry courtesy of the University of Houston. HONO was measured using a newly developed Laser Photofragmentation/Laser-Induced Fluorescence instrument (Bottorff et al., 2015; Bottorff et al., manuscript in preparation).

2.2 HO_x radical measurements

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 HO_2 or HO_2* (Dusanter et al., 2009a Griffith et al., 2013; 2016). In the LIF-FAGE technique, OH radicals are detected by laser-induced fluorescence after expansion of ambient air to low pressure. This extends the OH fluorescence lifetime, allowing temporal filtering of the fluorescence from laser scatter (Heard and Pilling, 2003). Ambient air is expanded through a 0.64 mm diameter orifice located at the top of a cylindrical nozzle (5 cm in diameter and 20 cm long), resulting in a flow rate of approximately 3 SLPM through the sampling nozzle. Two scroll pumps (Edwards XDS 35i) connected in parallel maintain a pressure inside the cell of 7.3 hPa.

The laser system used in this study consisted of a Spectra Physics Navigator II YHP40-532Q that produces approximately 8 W of radiation at 532 nm at a repetition rate of 10 kHz which is used to pump a Sirah Credo Dye laser (255 mg/L of Rhodamine 610 and 80 mg/L of Rhodamine 101 in ethanol), resulting in 40 to 100 mW of radiation at 308 nm. After exiting the dye laser, a fraction of the radiation is focused onto the entrance of a 12-m optical fiber to transmit the radiation to the sampling cell which was placed on top of the 1.8-m platform adjacent to the field lab. In the detection cell, the laser crosses the expanded air perpendicular to the flow in a White cell configuration with 24 passes. For this campaign, the laser power entering the sampling cell ranged from 0.5 to 4.4 mW and was monitored using a photodiode at the exit of the White cell. This does not reflect the laser power density inside the detection cell due to overlap of the beams in the multipass configuration.

OH radicals are excited and detected using the $A^2\Sigma^+ \upsilon' = 0 \leftarrow X^2\Pi \upsilon'' = 0$ transition near 308 nm (Stevens et al., 1994). The net signal is measured by spectral modulation by tuning the wavelength on- and off-resonance in successive modulation cycles. A reference cell where OH is produced by thermal dissociation of water vapor is used to ensure that the laser is tuned on and off the OH transition. The OH fluorescence is detected using a microchannel plate photomultiplier tube (MCP-PMT) detector (Hamamatsu R5946U-50), a preamplifier (Stanford Research System SR445) and a gated photon counter (Stanford Research Systems SR 400). The MCP-PMT is switched off during the laser pulse through the use of electronic gating allowing the OH fluorescence to be temporally filtered from laser scattered light. A Teflon injector located approximately 2.5 cm below the inlet and 17.5 cm above the detection axis allowed for the addition of NO (approximately 2 sccm, 1.4×10^{13} cm^{-3}, Matheson Gas, 10% in N_2) to convert ambient HO_2 to OH through the fast $HO_2 + NO \rightarrow OH + NO_2$ reaction, allowing for indirect measurements of HO_2.

The IU-FAGE instrument is calibrated by producing known quantities of OH and HO_2 from the photolysis of water vapor in air using a mercury penlamp within the calibration source as described previously (Dusanter et al., 2008). For these calibrations, zero air was sent through a humidifier and delivered at a flow rate of 38-50 L min^{-1} to the calibration source. Uncertainties associated with the UV water photolysis calibration technique have been described previously (Dusanter et al., 2008) and are estimated to be 18% (1σ) for both OH and HO_2.

2.2.1 Measurement of OH interferences

The LIF-FAGE measurements are subject to potential interferences where OH radicals are generated inside the detection cell. For example, ozone can be photolyzed by the laser and in the presence of water vapor can produce hydroxyl radicals (Davis et al., 1981a; 1981b) (reactions R1 and R2):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad \text{(R2)}$$

This interference in the IU-FAGE instrument is monitored through laboratory calibrations utilizing various concentrations of ozone, water vapor, and laser power. To characterize this and any other interference during ambient measurements, a chemical scrubbing technique is used to remove ambient OH prior to entering the detection cell (Griffith et al., 2016; Rickly and Stevens, 2018). This chemical modulation technique is used to monitor levels of the laser-generated ozone-water interference and any other processes that may produce OH radicals within the excitation axis.

Hexafluoropropylene (C_3F_6, 95.5% in N_2, Matheson) is added through a circular injector 1 cm above the nozzle with a flow rate of approximately 3.5 sccm to remove 95% of externally generated OH (Rickly and Stevens, 2018). During ambient measurements, chemical addition of C_3F_6 is modulated in between ambient OH measurements every 15 minutes for a duration of 10 minutes. The differences between the measured OH during C_3F_6 addition and OH measurements including the interference represents the net ambient OH concentration in the atmosphere. Taking the measurement of potential interferences into account results in a limit of detection for OH for this campaign of approximately 7.9×10^5 cm^{-3} for a 30 min average (S/N = 1).

2.2.2 Contribution of RO_2 interferences during HO_2 measurements

As discussed above, HO_2 radicals are measured indirectly after sampling ambient air at low pressure through chemical conversion to OH by addition of NO and subsequent detection of OH by LIF:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad \text{(R3)}$$

It was previously believed that the detection of HO_2 radicals using this technique was free from interferences from the reaction of RO_2 radicals with NO, as model simulations and measurements suggested that the rate of conversion of RO_2 radicals to HO_2 by reactions R4 and R5 and subsequent conversion to OH through reaction R3 were negligible. This was due to the slow rate of reaction R5 under the reduced oxygen concentration in the low pressure LIF-FAGE cell and the short reaction time between injection of NO and detection of OH (Heard and Pilling, 2003).

$$RO_2 + NO \rightarrow RO + NO_2 \qquad \text{(R4)}$$

$$RO + O_2 \rightarrow R'O + HO_2 \qquad \text{(R5)}$$

For example, RO_2 radicals produced from the OH-initiated oxidation of small alkanes were found to produce a negligible yield of HO_2 (Stevens et al., 1994; Kanaya et al., 2001; Tan, et al., 2001; Creasey et al., 2002; Holland et al., 2003).

However, recent laboratory studies have shown that there are interferences associated with measurements of HO_2 from the conversion of RO_2 radicals derived from the OH-initiated oxidation of alkenes and aromatics to HO_2 (and subsequently OH) by reaction with NO. The high conversion efficiency of alkene-based peroxy radicals to HO_2 is due to the ability of the β-hydroxyalkoxy radicals produced from OH + VOC reactions to rapidly decompose, forming a hydroxyalkyl radical which then reacts rapidly with O_2 leading to the production of a carbonyl compound and HO_2 (Fuchs et al., 2011; Whalley et al., 2013; Lew et al., 2018). Because of this interference, measurements of peroxy radicals that are sensitive to this interference are denoted as HO_2^* ($[HO_2^*] = [HO_2] + \alpha\,[RO_2]$, $0<\alpha<1$). The conversion efficiency depends on the instrumental characteristics and configurations employed as well as the amount of NO added. The RO_2-to-HO_2 conversion efficiencies for a number of different peroxy radicals have been characterized for current and past configurations of the IU-FAGE instrument (Lew et al., 2018). For the configuration of the IU-FAGE instrument used in this study, the conversion efficiency of isoprene-based peroxy radicals was found to be approximately 83%, while the conversion efficiency of propane peroxy radicals was found to be approximately 15%. A high concentration of NO leading to a high conversion efficiency of isoprene-based peroxy radicals to HO_2 was used throughout the study to provide a useful intercomparison of the IU-FAGE HO_2^* measurements with the RO_2+HO_2 measurements by the Drexel University Ethane – Nitric Oxide Chemical Amplifier (ECHAMP) instrument (Kundu et al., 2019), as HO_2 and isoprene-based peroxy radicals accounted for approximately 70% of the total peroxy radicals at this site (see below). To maximize measurement overlap for the intercomparison, low concentrations of added NO were not used and as a result no measurements of HO_2 with minimal interference from RO_2 radicals were obtained. The instrumental precision for the HO_2^* measurement based on the variability of the background signal due to laser scatter and detector noise results in a limit of detection for HO_2^* during this campaign of 7×10^7 cm^{-3} for a 30 second average (S/N =1).

2.3 OH reactivity measurements

The IU Total OH Loss rate Method (TOHLM) instrument is based on the method of Kovacs and Brune (2001) and is described in detail elsewhere (Hansen et al., 2014). Briefly, the instrument is comprised of a flow tube reactor measuring 5 cm in diameter and 75 cm in length. Ambient air is introduced through an 8 cm diameter perfluoroalkoxy polymer film hose attached to the flow tube at a flow rate of approximately 180 SLPM using a regenerative blower (Spencer VB001) to establish turbulent flow conditions. Previous measurements have demonstrated that different lengths of this inlet tubing do not significantly impact the measured OH reactivity (Hansen et al., 2014). A pitot-static tube (Dwyer Instruments) is positioned just before the exit of the flow tube facing the turbulent core of the flow, approximately 1 cm from the flow tube wall. The pitot-static tube is connected to a differential pressure gauge (MKS Instruments) to measure the total flow tube velocity.

OH radicals are produced in a movable injector that houses a mercury pen lamp (UV Pen-Ray) in which the top of the pen lamp was positioned at the end of the injector, just before a spiral Teflon spray nozzle used to promote mixing within the flow tube (McMaster Carr). In addition, a turbulizer is attached to the injector tube 24 cm before the spray nozzle consisting of four 1 cm wide fins to promote turbulent flow conditions as well as to provide support of the injector throughout the flow tube. The injector is inserted along the main axis and is configured for automated movement acquiring continuous measurements in the forward and backward directions. A nitrogen flow of 10 standard liters per minute (SLPM) is bubbled through high-purity water (EMD Chemicals) producing water vapor which is directed through the injector and photolyzed by the penlamp to produce OH with typical concentrations on the order of 10^9 cm^{-3}. This method is known to also produce HO_2 radicals, which can lead to a regeneration of OH at NO mixing ratios greater than 1 ppbv (Kovacs and Brune, 2001). However, because the average NO mixing ratio measured over the course of the campaign was below this value, no correction to the measured reactivity was applied (Hansen et al., 2014).

OH radicals were measured using a similar FAGE detection cell described above. Ambient air was expanded through a 1 mm diameter orifice to a total pressure of approximately 8 hPa. OH radicals were excited by a portion of the 308 nm output of the dye laser, with the resulting fluorescence detected by a gated channel photomultiplier tube detector (Excelitas MP 1300) and monitored by a photon counter (Stanford Research SRS 400). A 2 meter long optical fiber was used to transmit the 308-nm laser beam to the OH reactivity detection cell which was located inside the field lab. The laser power was measured at the exit of the detection cell and monitored with a photodiode.

As ambient air entered the flow tube, the automated OH source injector allowed for varying reaction time with the ambient air over a distance of approximately 15 cm for a period of 2.5 minutes. This produced an OH decay over a reaction time of 0-0.15 s from which the OH reactivity was determined. Losses of OH on the walls of the flow tube were measured by flowing high-purity nitrogen (Indiana Oxygen) at 180 SLPM through the flow tube in addition to the OH production through the injector to measure the decay of OH in the absence of any VOCs. Several measurements of this wall loss (k_b) resulted in an average value of 10 ± 2 s^{-1} (1σ).

The calculated OH reactivity for a measured compound X (k_X), can be determined from the product of the concentration of X and its second-order rate constant with OH:

$$k_X = k_{OH+X}[X] \tag{1}$$

Summation of this value for each reacting species gives the total OH reactivity (k_{OH}):

$$k_{OH} = \sum_i k_{OH+X_i}[X_i] \tag{2}$$

Under pseudo-first order conditions ([OH]<<[X]), the OH concentration within the flow tube can be expressed as a first-order exponential decay:

$$[OH]_t = [OH]_0 e^{-(k_{OH}+k_b)t} \tag{3}$$

Solving for k_{OH}, the OH reactivity, gives:

$$k_{OH} = -\frac{\Delta \ln[OH]}{\Delta t} - k_b \tag{4}$$

Measurements of the change in the concentration of OH over the reaction time produces the measured OH reactivity value. These measurements can be compared to the calculated total reactivity from measured OH sinks (Eq. 2) to determine whether the measured total OH reactivity can be accounted for by the measured sinks. The difference between the measured and calculated total OH reactivity is referred to as the "missing" OH reactivity.

Laboratory measurements of the reactivity of several VOCs with well-known rate constants, including butane, isoprene, and propane showed that the OH reactivity measurements for these compounds were on average 30% lower than calculated when the measured velocity of the turbulent core is used to determine the reaction time. This consistent underestimation of the OH reactivity is likely due to either incomplete mixing of the reactants or a systematic underestimation of the reaction time, and is similar to that measured previously by Hansen et al. (2014). As a result, the measured ambient OH reactivity values were scaled by a factor of 1.41. Measurements performed over a range of OH reactivity values suggest that the IU-TOHLM instrument can measure OH reactivity up to 45 s^{-1} with a precision (1σ) of 1.2 s^{-1} + 4% of the measured value for a 10 min average (Hansen et al., 2014).

2.4 Modeling HO_x concentrations and OH reactivity

Ambient measurements of OH, HO_2*, and total OH reactivity were modeled with the Regional Atmospheric Chemistry Mechanism (RACM2) (Goliff et al., 2013) and the Master Chemical Mechanism version 3.2 (Jenkin et al., 1997; Saunders et al., 2003). 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 HO_x radical production, and includes the LIM1 updated bulk isomeration rate constants described in Peeters et al. (2014) leading to the formation of HO_2 and hydroxyperoxy aldehydes (HPALDs) which can photolyze leading to OH production. 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 HO_x recycling from peroxy radical H-shift isomerization reactions (Jenkin et al., 2015). The bulk peroxy radical isomerization rate constants in MCM 3.3.1 are based on the recommendations of Peeters (2015), which are approximately a factor of 5 lower than the original LIM1 recommended rates (Novelli et al., 2020) in order to bring the model predictions into better agreement with experimental measurements of the production of HPALDs and other products (Crounse et al., 2011; Teng et al., 2017; Wennberg et al., 2018; Berndt et al., 2019).

The Framework for 0-D Atmospheric Modeling (F0AM) was used to calculate the radical concentrations and OH reactivity observed at the IRRONIC site (Wolfe et al., 2016). The model was constrained by the 30 minute average measured mixing ratios of ozone, NO_x, and VOCs and processed through a 5 day spin-up to generate unmeasured secondary oxidation products. Table S1 summarizes the measured compounds and includes their grouping into the condensed RACM2 model inputs. Because the VOC measurements occurred every 90 minutes, the measurements were interpolated into 30 min bins before input to the model. Due to the minimal overlap of the NO measurements with the HO_x measurements, the model was only run for the days when there was measurements of NO, limiting the number of days for comparison with the radical measurements. 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 NO_x-O_3-radical chemistry necessitate using constrained measurements of NO, NO_2, and O_3. The measured J(NO_2) was used to scale the model calculated J(NO_2) and other photolysis rates. The model uncertainty is approximately 30% (1σ), estimated from uncertainties associated with the input parameters and the rate constants for each reaction (Griffith et al., 2013; Wolfe et al., 2016).

3 Results and discussion

Campaign diurnal average measurements of J(NO_2), temperature, isoprene, O_3, NO_2, and NO are summarized in Fig. 1. The maximum average mixing ratio of NO of approximately 315 ppt was observed at approximately 08:00 (EDT), while the average mixing ratio of NO_2 reached a maximum of 2 ppb around 10:00. Average mixing ratios of isoprene ranged from 0.4 to 4.4 ppb, reaching a maximum around 18:00. The relatively high nighttime mixing ratios often observed at this site are likely due to the fact that the measurements were made below the forest canopy and relatively close to the surface. As a result, vertical stratification likely resulted in higher concentrations of isoprene near the surface during several nights, similar to other measurements of biogenic VOCs below the forest canopy (Bsaibes, et al., 2020). Anthropogenic VOCs were relatively low at this site, with maximum mixing ratios of benzene less than 80 ppt. Day-to-day profiles (July 10 to July 25) are illustrated in Fig. 2, showing measurements of O_3, temperature, isoprene, NO_x, HO_2*, and OH. Unfortunately, instrumental problems limited the NO measurements prior to 19 July.

3.1 OH measurements and model comparison

OH concentrations were determined using the chemical modulation technique described above using external C_3F_6 addition to scavenge ambient OH and measure interferences producing OH inside the IU-FAGE detection cell, including laser generated OH. The measured interferences were subtracted from the total OH signal determined from spectral modulation, resulting in net ambient OH concentrations (Fig. 2). As can be seen from this figure, the measured interference was a significant fraction of the total OH signal on many days.

Figure 3 illustrates the total measured OH radical signal by spectral modulation (black circles), the measured interference (blue squares), and the expected laser-generated interference from reactions 3 and 4 calculated from laboratory calibrations (Griffith et al., 2016) (green points) during 14 July and 15 July. On 15 July, the measured interference was similar to the calculated interference suggesting that the majority of the measured interference was laser-generated. However, on 14

July, the measured interference was much larger than the calculated interference, suggesting that the majority of the measured interference was due to an unknown source. Subtraction of the calculated laser-generated interference from the measured interference on all days resulted in a measurement of the unknown interference that increased with both ozone and temperature during the campaign (Fig. 4).

This result is consistent with the observations from Mao et al. (2012) who found that the interference measured in their LIF-FAGE instrument using a similar chemical modulation technique increased with ozone and total OH reactivity. The observed increase in the magnitude of the unknown interference with ozone and temperature suggests that the interference may be related to the ozonolysis of biogenic VOCs, whose emissions increase with temperature. This result is also consistent with the measurements of Novelli et al. (2017), who found that their observed interference correlated with the product of ozone and biogenic VOC concentrations, although the correlation in the present study was weak ($R^2 = 0.15$). Previous measurements have shown that some LIF-FAGE instruments, including the IU-FAGE instrument, are susceptible to an interference under high concentrations of ozone and biogenic VOCs, perhaps due to the decomposition of Criegee intermediates inside the FAGE detection cell (Novelli et al., 2014; Fuchs et al., 2016; Novelli et al., 2017; Rickly and Stevens, 2018). However, estimated concentrations of Criegee intermediates in similar environments on the order of 5×10^4 cm^{-3} (Novelli et al., 2017) are too low to explain the observed interference during the IRRONIC campaign.

The observation of a significant interference during this campaign is in contrast to previous measurements of OH by the IU-FAGE instrument in a forested environment during the CABINEX 2009 campaign (Griffth et al., 2013). During this campaign, several tests were conducted where C_3F_6 or CO was added to remove ambient OH. These tests did not reveal any significant interference, and measurements of OH were found to be in good agreement with model predictions (Griffith et al., 2013). One possible explanation for this discrepancy with the measurements during IRRONIC is the lower levels of ozone and temperatures observed during CABINEX compared to IRRONIC. Average mixing ratios of ozone during CABINEX were near 30 ppb and average temperatures were near 20ºC during the day, with average mixing ratios of isoprene less than 2 ppb in the afternoon. These levels of ozone and temperature are lower than that where the interference was observed during IRRONIC (Fig. 4), suggesting that a similar interference was likely undetectable during CABINEX.

Recent measurements have found that NO_3 radicals can lead to an interference in FAGE instruments (Fuchs et al., 2016), although the mechanism for production of this interference is not known. Such an interference in the IU-FAGE instrument could explain the observed interference during some nights (Fig. 3), but is unlikely the source of the interference during the daytime. Another possible source of the interference is the decomposition of ROOOH molecules inside the FAGE detection cell formed from the reaction of OH with RO_2 radicals (Fittschen et al., 2019). However, assuming a rate constant of 1×10^{-10} cm^{-3} s^{-1} for the OH + RO_2 reaction, it is unlikely that a significant fraction of RO_2 radicals will react to form ROOOH under the mixing ratios of NO observed at this site, as the estimated lifetime of RO_2 radicals with respect to reaction with NO was an order-of-magnitude shorter than that for reaction with OH. Additional measurements and laboratory tests will be needed to identify and minimize interferences associated with LIF-FAGE measurements of OH.

The day-to-day measurements of OH after the interference has been subtracted for 10-20 July and 24-25 July are also illustrated in Fig. 2. Because the interference was not measured simultaneously as the ambient OH measurements, subtraction of the measured interference often resulted in both apparent negative concentrations as well as large positive concentrations at night. These large positive and negative values reflect the fact that the nighttime measurements of the interference was much greater than the ambient OH signals and was highly variable between measurement cycles (Fig. 3), resulting in an ambient OH measurement uncertainty that was sometimes larger than the precision calculated from a quadratic propagation of the errors associated with the individual measurements of the ambient OH plus the interference and the interference alone. Measurements on 21-22 July focused on measurements of HO_2* 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. This figure also illustrates the day-to-day model results for OH and HO_2* for the days when NO was also measured simultaneously, showing the MCM 3.3.1 and the RACM2-LIM1 models for simplicity.

Figure 5 (top) shows the average diurnal profile of the 15-min OH measurements, both with and without the measured interference, binned into 1 hour time periods for all the days illustrated in Fig. 2 (left panel), and binned into 2 hour time periods along with the MCM and RACM model results for the days when NO was measured simultaneously (right panel). The average ambient diurnal OH radical concentration measured during the entire campaign reached a maximum of approximately 4-5 × 10^6 cm^{-3} after the measured interference was subtracted (Fig. 5, top left), and was slightly lower during the period when NO measurements were available (Fig. 5, top right). If the measured interference was not subtracted from the total OH signal determined by spectral modulation, the resulting OH radical concentrations would be as high as 9 × 10^6 cm^{-3} (Fig. 5), much greater than the MCM and RACM2 modeled diurnal average maximum concentrations of approximately 2-3 × 10^6 cm^{-3}. The daytime OH radical concentration measurements after the interference has been subtracted are in better agreement with the model results. Including versions of the LIM1 mechanism for HO_x regeneration in both the MCM (3.3.1) and RACM2 (RACM2-LIM1) models result in higher modeled daytime concentrations of OH compared to the base MCM 3.2 and RACM2 mechanisms, with the RACM2-LIM1 results within 30% of the measured concentrations during the day (9:00-17:00 EDT) when NO was measured simultaneously (Fig. 5, top right), while the MCM 3.3.1 model underpredicted the measurements during this period by approximately a factor of 2. These results are similar to that found by Novelli et al. (2020), who found that the MCM 3.3.1 underpredicted measurements of OH by a factor of approximately 1.4 during isoprene oxidation experiments in the SAPHIR chamber. The measured OH concentrations could be reproduced using a model that increased the yield of HPALD in the oxidation mechanism, resulting in an effective bulk isoprene peroxy radical isomerization rate similar to that in the original LIM1 mechanism (Novelli et al., 2020). These larger bulk peroxy radical isomerization rates are incorporated into the RACM2-LIM1 mechanism used in the present study (Tan et al., 2017), leading to the higher modeled radical concentrations compared to the RACM2 and MCM model results shown in Fig. 5.

Although the RACM2-LIM1 mechanism appears to be able to reproduce the daytime OH radical measurements compared to the MCM 3.3.1 mechanism, all the models underestimate the measurements in the early evening and night. While there is uncertainty associated with these nighttime measurements due to the large interference that was subtracted, similar concentrations of OH were observed during the evening by both the IU-FAGE instrument and the University of Colorado Chemical Ionization Mass Spectrometry (CIMS) instrument at this site in 2017 during an informal instrument intercomparison (Rosales et al., 2018; Reidy et al., 2018). These results suggest that there may be a missing radical source during this period, such as the ozonolysis of unmeasured biogenic VOCs, and additional measurements will be required to resolve this discrepancy.

3.2 HO_2* measurements and model comparison

The day-to-day measurements of HO_2* are also illustrated in Fig. 2 with the MCM 3.3.1 and RACM2-LIM1 model results for the days when NO was also measured simultaneously. Figure 5 shows the average diurnal profile of the HO_2* measurements for all the days illustrated in Fig. 2 (left panel, bottom) which were similar to the measured HO_2* concentrations for the days when NO was measured simultaneously, along with the MCM and RACM model results (right panel, bottom). The contribution of modeled RO_2 radicals to the modeled HO_2* is based on laboratory calibrations of the RO_2–to–HO_2 conversion efficiencies for the sampling conditions used in this study (Lew et al., 2018) and are incorporated into both versions of the RACM2, and MCM peroxy radical categories. Under the instrumental conditions during the campaign, the conversion efficiency of isoprene-based peroxy radicals to HO_2 was determined to be approximately 83 ± 7%, while the conversion efficiency of methyl peroxy radicals was estimated to be approximately 5% (Lew et al., 2018). These two peroxy radicals accounted for the majority of RO_2 radicals predicted by the models (see below). The maximum measured HO_2* concentration each day during the campaign was generally between approximately 2×10^8 and 2×10^9 molecules cm^{-3} (Fig. 2), with an average daily maximum value of approximately 1×10^9 cm^{-3} (Fig. 5). The RACM2-LIM1 and MCM 3.3.1 modeled diurnal averaged HO_2* reached a maximum of approximately 1.4×10^9 cm^{-3} and 1.0×10^9 cm^{-3}, respectively, compared to values of 1.2×10^9 cm^{-3} and 1.0×10^9 cm^{-3}, respectively, for the RACM2 and MCM 3.2 modeled HO_2* (Fig. 5).

The predicted HO_2*concentrations by the base RACM2 model are in good agreement with the measured concentrations when NO was measured simultaneously, with the model results within approximately ±10% of the measurements on average and within the calibration uncertainty of the measurements (38%, 2σ). Including the LIM1 mechanism in the RACM2 mechanism increases the modeled HO_2* by approximately 15-20% due to the modeled increase in HO_x radical production from the isomerization of isoprene-based peroxy radicals, overpredicting the measurements by approximately 10-30%. These results are in contrast to that observed during the CABINEX campaign, where a RACM-based model overpredicted the measured HO_2* by as much as a factor of 2 (Griffith et al., 2013), likely related to the higher concentrations of NO observed during IRRONIC compared to CABINEX increasing the importance of the HO_2 + NO and RO_2 + NO reactions in determining the fate of these radicals. The MCM-based model results are also in good agreement with the measured HO_2* (Fig. 2 and 5). The MCM 3.3.1 and 3.2 mechanisms predicted HO_2* concentrations are approximately 5-30% less than the measurements between 12:00-18:00 EDT but within the calibration uncertainty of the measurements, with the MCM 3.3.1 mechanism predicting slightly greater concentrations due to the inclusion of HO_x production from the isomerization of isoprene-based peroxy radicals.

The RACM2-LIM1 and MCM 3.3.1 diurnal average modeled HO_2* concentrations and the model contribution of peroxy radicals to HO_2* are shown in Fig. 6 (left panels). The diurnal profile of the HO_2* radical concentration predicted by these models includes contributions primarily from isoprene peroxy radicals and HO_2 radicals, with smaller contributions from methyl peroxy and acetyl peroxy radicals (Fig. 6). The RACM2 and MCM 3.2 models produced similar results, with HO_2 and isoprene peroxy radicals contributing to the majority of the modeled HO_2* concentrations (Fig. S1). The total modeled RO_x (RO_2 + HO_2) concentrations by the different mechanisms are also shown in Fig. 6 (right panels). The RACM2-LIM1 model predicted that the diurnal average total RO_x concentration consisted primarily of HO_2 (42%), isoprene peroxy radicals (30%), methyl peroxy (CH_3O_2, 14%), and acetyl peroxy (CH_3CO_3, 4%), with daytime (08:00 – 20:00) contributions of 42%, 32%, 13%, and 4% for HO_2, isoprene peroxy, CH_3O_2, and CH_3CO_3, respectively. The MCM 3.3.1 model predicted that HO_2 (43%), isoprene peroxy (18%), methyl peroxy (14%), acetyl peroxy (4%) were the major contributors to the modeled diurnal average total RO_x concentration, with daytime contributions of 43%, 20%, 13%, and 4% (Fig. 6). Similar results were obtained from the MCM 3.2 and RACM2 models (Fig. S1). As discussed above, the configuration of the IU-FAGE instrument used in this study converted approximately 83% of isoprene peroxy radicals to HO_2 upon addition of NO and minimally converts methyl peroxy radicals to HO_2 (<5%) (Lew et al., 2018). Thus, the majority of the contributing species to the measured HO_2* are HO_2 and isoprene peroxy radicals which together account for approximately 70% of the total peroxy radical concentration predicted by these models. Measurements of the total HO_2 + RO_2 radical concentrations using an Ethane – Nitric Oxide Chemical Amplifier (ECHAMP) were found to be in good agreement with the HO_2* measurements reported here and are summarized in Kundu et al. (2019).

3.3 Total OH reactivity measurements and model comparison

The measured total OH reactivity and that calculated from measured OH sinks using both the RACM and MCM mechanisms are shown in Fig. 7, where the measured OH reactivity is averaged into 2 hour bins. As illustrated in this figure, the calculated OH reactivity was in relatively good agreement with the measured OH reactivity on some days and nights, specifically 15-16 July, with missing reactivity observed later in the campaign. Overall, the averaged measured OH reactivity varied between the instrumental limit of detection of 1 s^{-1} to a maximum of approximately 31s^{-1} with an overall diurnal average value of approximately 13 s^{-1}.

The campaign diurnal averaged measured OH reactivity is shown in Fig. 8 along with the calculated total OH reactivity from the measured OH sinks. As expected for this deciduous forest environment, isoprene was the dominant contributor making up 37% of the diurnally averaged total reactivity, followed by OVOCs (28%), inorganics (10%), alkanes and alkenes (5%), anthropogenic non-methane hydrocarbons (NMHC) (1%), and monoterpenes (<1%) with missing reactivity accounting for the remaining 18% (Fig. S2). During the daytime (08:00 and 20:00) the contributions are similar, with isoprene being the largest contributor at 47% followed by OVOCs (24%), inorganics (8%), alkanes and alkenes (4%), anthropogenic

NMHC (1%), and monoterpenes (<1%) with missing reactivity accounting for the remaining 14%. During the nighttime, (20:00 to 08:00), OVOCs were the dominant contributor to the modeled OH reactivity at 32% followed by isoprene (24%), inorganics (11%), alkanes and alkenes (6%), anthropogenic NMHC (2%), and monoterpenes (<1%) with missing reactivity of 24% (Fig. S2).

The campaign diurnal average (Fig. 8) shows a correlation with temperature, with the maximum average OH reactivity of approximately 20 s^{-1} occurring around 13:30. The calculated reactivity was consistent with the measured reactivity for temperatures less than 294 K, while the observed reactivity is greater than that calculated from the measured sinks for higher temperatures, although at temperatures above 302 K the measured reactivity appears to be less than calculated (Fig. S3). These results are similar to several previous studies in which the measured missing reactivity appeared to increase with temperature (Di Carlo et al., 2004; Hansen et al., 2014; Bsaibes, et al., 2020).

Figure 8 also shows the campaign average OH reactivity including the reactivity of unmeasured oxidation products predicted by the MCM 3.3.1 model. On average, including the contribution of unmeasured oxidation products can account for the majority of the missing reactivity. While the model tends to overpredict the average measured reactivity in the afternoon and evening, the model results agree to within the combined uncertainty of the model and the precision of the measurement (Hansen et al., 2014). Similar results were obtained by the RACM2 models, although the predicted reactivity of unmeasured oxidation products by the RACM2 models are approximately a factor of two smaller than that predicted by the MCM models (Fig. S4). These results suggest that the models are generally able to reproduce the measured OH reactivity at this site, and that the missing reactivity observed during IRRONIC may be due to unmeasured oxidation products, with isoprene nitrates and isoprene epoxides within the RACM2 and MCM mechanisms being the primary contributors to the missing reactivity.

While the campaign averaged OH reactivity measurements appear to be in reasonable agreement with the calculated reactivity based on measured compounds, there were several days that displayed large missing reactivity similar to that observed by Hansen et al. (2014). The MCM 3.3.1 model results for a day with the largest missing reactivity (17 July) is shown in Fig. 9, indicating that the modeled reactivity including unmeasured oxidation products cannot explain the observed reactivity on this day. 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.

3.4 Radical budgets

The analysis of the rates of radical initiation, propagation, and termination can provide insight to the importance of individual radical sources and sinks. For the IRRONIC campaign, the OH radical budget is illustrated in Fig. 10, where OH radical production reactions are represented in shades of blue and loss reactions are represented in shades of red. Daytime production includes reactions with both initiation and propagation that produces OH radicals (positive rates), while daytime

OH loss reactions are represented by propagation and termination reactions that remove OH (negative rates). For simplicity only the RACM2 and RACM2-LIM1 radical budgets are shown.

The maximum rates for the OH radical budget of approximately 5 × 10^7 cm^{-3} s^{-1} from the RACM2-LIM1 model were higher than the maximum value of approximately 4 × 10^7 cm^{-3} s^{-1} in RACM2. The addition of the LIM1 mechanism increases the OH radical production rate mostly from photolysis of hydroxyperoxy aldehydes (HPALD) produced from the isomerization of isoprene-based peroxy radicals and their subsequent chemistry (Peeters et al., 2014; Tan et al., 2017). In the RACM2-LIM1 model, the daytime OH radical production is dominated by the HO_2 + NO reaction from 10:00 to 14:00 (66%) and drops to 47% from 14:00 to 18:00. Ozone photolysis and the LIM1 mechanism contribute up to 18-24% and 8-15% of the total OH radical production during the morning and afternoon, with ozonolysis (VOC+O_3) and photolysis of HONO, H_2O_2, methacrolein (MACR), and organic peroxides (OP1, OP2) contributing to 4-7% and 4-6% of the total OH radical production (Fig. 10). A majority of the OH radical loss is due to OH reactions with VOCs (65-72%) and OVOCs (27-23%) during the morning and afternoon. As described above, the measured total OH reactivity was in reasonable agreement with the modeled OH reactivity; therefore, it is likely that the total OH loss is well represented in the model. An experimental radical budget for the period when the measurements were complete suggests that the total measured OH production rate during the day is nearly balanced by the total OH loss rate based on the measured total OH reactivity (Fig. S5), consistent with the agreement between the measured and modeled OH on these days as discussed above and within the combined uncertainties of all the measurements (38% (2σ) for OH and for HO_2* for example), similar to that observed previously (Tan et al., 2019). However, the experimental budget is not balanced in the evening, suggesting that there may be a missing radical source during this period, consistent with the model underprediction of the OH measurements discussed above.

The total radical (RO_x) budget from the RACM2 mechanisms of OH, HO_2, and RO_2 radicals is illustrated in Fig. 11. Overall, total radical initiation in the RACM2-LIM1 mechanism was larger, with a maximum value of approaching 3 × 10^7 cm^{-3} s^{-1} compared to RACM2 maximum value of approximately 2 × 10^7 cm^{-3} s^{-1}. The increase in total radical initiation in the RACM2-LIM1 model is due to both the added radical initiation from the photolysis of HPALDs as well as increased radical initiation from other aldehydes produced in the LIM1 mechanism. Overall, radical initiation from the photolysis of HPALDs and the subsequent chemistry from the LIM1 mechanism contributed 16-22% of total radical initiation during the morning and afternoon, while photolysis of formaldehyde and other aldehydes together contributed to approximately 42% of total radical initiation, with ozone photolysis contributing to 29-33% of radical initiation (Fig. 11). In contrast, ozone photolysis contributes to approximately 44-46%% of radical initiation in the RACM2 mechanism, with formaldehyde and other aldehydes together contributing 43% (Fig. 11). Radical termination for both mechanisms is dominated by peroxy radical self-reactions, such as the HO_2 + HO_2 reaction, as well as the reaction of HO_2 with isoprene-based peroxy radicals (ISOP) and other peroxy radicals (RO_2). These reactions account for approximately 67-95% of radical termination due to the low levels of NO_x used in the models, with reaction of OH +NO_2 and other NO_x radical reactions accounting for approximately 5-33% of radical termination in these models during the day (Fig. 11).

The partitioning of the total radical budget production for IRRONIC is similar to the modeled budget observed during PROPHET 2008 and CABINEX 2009 (Griffith et al., 2013). The updated RACM model used during these campaigns predicted that radical termination was dominated by HO_2 + RO_2 reactions (including the HO2 + ISOP reaction), contributing to approximately 80% of total radical termination, similar to the 67-84% for the HO_2+ISOP, HO_2+RO_2 , and HO_2+HO_2 reactions predicted here by the RACM2 model. The photolysis of ozone accounted for approximately 20-30% of total radical initiation during these campaigns based on an updated version of the RACM model (Griffith et al., 2013) compared to approximately 45% predicted by the RACM2 mechanism during IRRONIC due to higher concentrations observed during this campaign. Ozonolysis reactions contributed to approximately 20-30% of total radical initiation during PROPHET and CABINEX compared to approximately 12% during IRRONIC. Photolysis of HCHO contributed to approximately 22-24% of the total rate of radical initiation during IRRONIC compared to 23% and 5% during PROPHET 2008 and CABINEX 2009, respectively, with the low contribution during CABINEX primarily due to the lower mixing ratios of HCHO observed during this campaign (Griffith et al., 2013). In contrast, photolysis of HONO was a significant radical source during PROPHET and CABINEX, contributing 14-17% of radical initiation compared to approximately 3% of total radical production during IRRONIC due to the lower mixing ratios of HONO observed during IRRONIC. On average, mixing ratios of HONO during IRRONIC were approximately 40 ppt at night decreasing to approximately 10 ppt during the day (Fig. S6) compared to daytime mixing ratios between 50 and 75 ppt during PROPHET and CABINEX (Griffith et al., 2013). The reason for the difference in the measured HONO values between these two sites is unclear, but may be related to increased production from photolysis of nitric acid on the forest canopy surfaces at the PROPHET site (Zhou et al., 2011).

4 Summary

Measurements of OH radical concentrations using the IU-FAGE instrument during the IRRONIC campaign revealed a significant unknown interference that appeared to correlate with both temperature and ozone. The average measured OH radical concentration after the interference was subtracted reached an average daytime maximum of approximately 4-5 × 10^6 cm^{-3}. This is in contrast to the measurements including the interference which reached an average daytime maximum of approximately 9 × 10^6 cm^{-3}. Similar concentrations of OH were observed after any measured interference was subtracted at this site in 2017 during an informal intercomparison between the IU-FAGE instrument and the University of Colorado Chemical Ionization Mass Spectrometry (CIMS) instrument (Rosales et al., 2018; Reidy et al., 2018).

After subtracting the interference, the OH measurements were in better agreement with model simulations utilizing the Regional Atmospheric Chemical Mechanism 2 (RACM2) with an updated Leuven Isoprene Mechanism (LIM1) as well as the Master Chemical Mechanism versions 3.2 and 3.3.1. Both the RACM2-LIM1 and MCM 3.3.1 mechanisms add radical recycling reactions for isoprene oxidation that increase the modeled OH and peroxy radical concentrations. Similar to the results of Novelli et al. (2020), the RACM2-LIM1 model results were in better agreement compared to the MCM 3.3.1 mechanism, predicting maximum daytime OH concentrations that were within 30% of the measurements, likely due to a larger bulk isoprene peroxy radical isomerization rate leading to a greater rate of radical production. However, the models tend to underpredict the measured concentrations during the evening, suggesting that a significant radical source may be missing from the models. Additional measurements are needed in order to resolve this discrepancy. Nevertheless, it is clear that if the measured interference was not taken into account, the apparent OH concentrations would have been a factor of 2-4 greater than predicted by the model mechanisms, comparable to previous measurements under low NO_x and high isoprene conditions (Rohrer et al., 2014). These results are similar to that reported by Mao et al. (2012) and Mallik et al. (2017) who found good agreement between their OH measurements and model predictions when measured interferences were taken into account. Because of differences in instrument design (geometry, cell pressure, flow, etc.) these interferences may not significantly impact other LIF-FAGE instruments. However, future OH measurements using the LIF-FAGE technique should include methods to quantify potential instrumental artifacts even if they are insignificant, to demonstrate that the measurements are free from interferences.

Measurements of total OH reactivity were in reasonable agreement with that calculated from measured OH sinks, with isoprene contributing approximately 37% and OVOCs 28% of the diurnally averaged measured reactivity, with 18% of the measured reactivity missing. However, on average the missing reactivity fraction can be explained by unmeasured oxidation products, specifically from isoprene nitrates and isoprene epoxides within the RACM2 and MCM mechanisms. This indicates that these mechanisms are accurately representing the total OH loss at this site.

Measurements of HO_2 radicals by the IU-FAGE instrument using chemical conversion to OH by addition of NO has been shown to be sensitive to alkene-based peroxy radicals (Lew et al., 2018). As a result, the measurements represent a sum of HO_2 and a fraction of RO_2 radicals in the atmosphere (HO_2*). During the IRRONIC campaign, the measured HO_2* concentration primarily reflected the sum of HO_2 and isoprene-based peroxy radicals, which contributed to approximately 70% of the total modeled peroxy radicals. The average daytime ambient HO_2* measurements reached maximum concentrations of approximately 1×10^9 cm^{-3}. Both MCM models predicted HO_2* concentrations that were within 10-30% but generally lower than the measurements, while the RACM mechanisms resulting in predicted concentrations that were within 10-30% but generally greater than the measurements. However, all models predicted concentrations that were within the combined uncertainty of both the model and the measurement. These results are in contrast to some previous measurements in forest environments where model predictions were found to be significantly greater than measured HO_2* concentrations (Griffith et al., 2013), perhaps as a result of the lower mixing ratios of NO observed at these sites. Additional measurements are needed in order to resolve this discrepancy, which may be related to a gap in our understanding of peroxy radical chemistry under low NO conditions.

Data availability. Data are available upon request from the corresponding author (pstevens@indiana.edu).

Competing interests. The authors declare that they have no conflicts of interest.

Author contributions. PS, SD and EW designed the research project. ML, PR, BB, and PS were responsible for the LIF-FAGE OH, HO_2*, OH reactivity, and HONO measurements. SK and EW were responsible for the supporting measurements of NO, NO_2, and O_3. SD, SS, TL, and NL were responsible for the measurements of VOCs and OVOCs. ML, PR, ER, and PS conducted the analysis and photochemical modelling and wrote the paper with feedback from all co-authors. ML and PR contributed equally to the paper.

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Table 1: Measurements conducted during the IRRONIC field campaign.

Measurement	Instrument	Technique	LOD	Reference
OH HO_2*	LIF-FAGE	Laser-induced fluorescence – fluorescence assay by gas expansion	8×10^5 cm^{-3} / 30 min 7×10^7 cm^{-3} / 20 s	Dusanter et al., 2009a; Lew et al., 2018[a]
NO	Thermo 42i-TL	Chemiluminescence	50 ppt / 2 min	
NO_2	Aerodyne CAPS	Cavity attenuated phase shift spectroscopy	40 ppt / 10 s	
Ozone	2B Technologies Model 202	UV absorbance	3 ppb / 10 s	
OH reactivity	LIF-TOHLM	Total OH Loss Measurement	1 s^{-1} (10 min)	Hansen et al., 2013
HONO	LP LIF-FAGE	Laser-photofragmentation laser-induced fluorescence	20 ppt (30 min)	Bottorff et al., in prep
NMHCs	Online GC/FID	Gas chromatography with flame ionization detection	10-100 ppt (1.5 hr)	Badol et al., 2004
OVOCs	Online GC/FID-MS	Gas chromatography with mass spectrometer and FID	5-100 ppt (1.5 hr)	Roukos et al. (2009)
	Off-line Sorbent GC-MS	Sorbent cartridges analyzed by GC-MS		Detournay et al. (2011); Ait-Helal et al. (2014)
	Off-line DNPH HPLC-UV	Dinitrophenylhydrazine cartridges analyzed by high-performance liquid chromatography with UV detection		
$J(NO_2)$		Spectral Radiometry	0.3×10^{-4} s^{-1}	Shetter and Muller (1999)

[a] HO_2* = HO_2 plus a fraction of certain RO_2 radicals (see text)

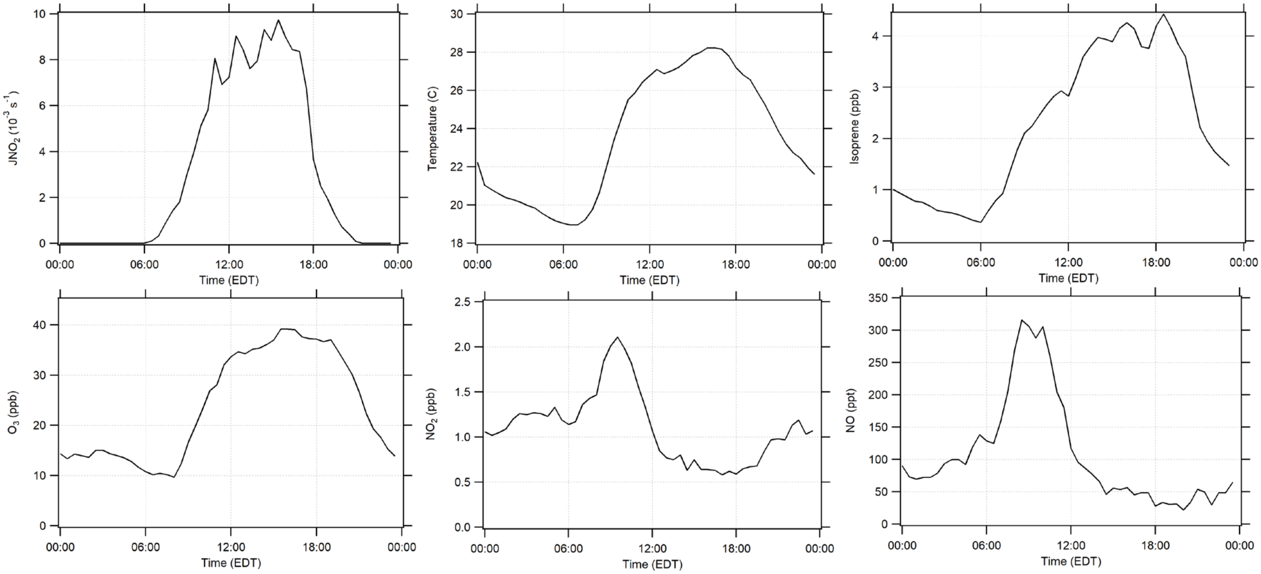

Figure 1. Diurnal campaign average profiles of J(NO$_2$), temperature, isoprene, O$_3$, NO$_2$, and NO.

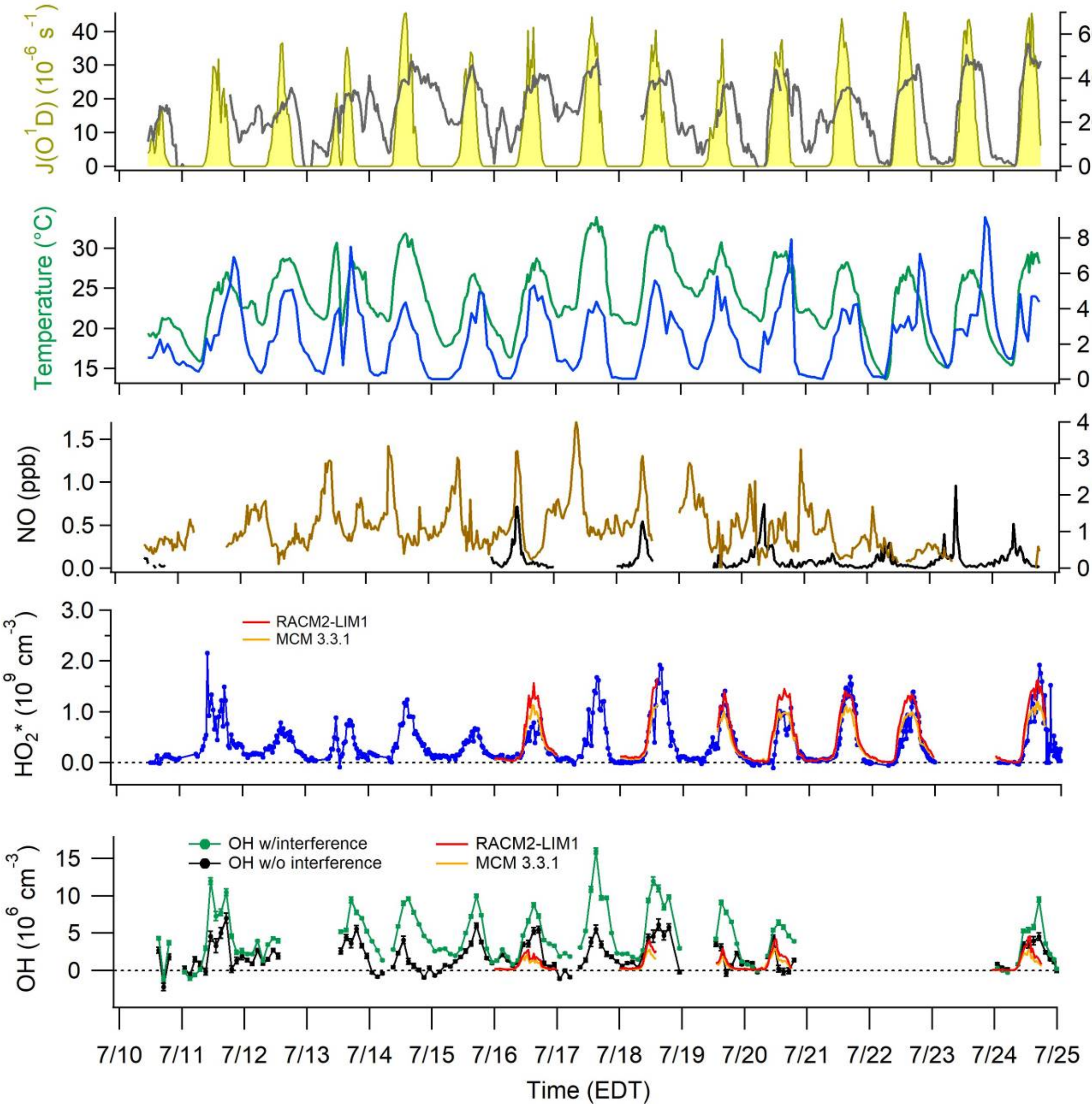

Figure 2. Time series of OH and HO$_2$* from July 10 to July 25 with model calculated J(O^{1}D) scaled to the measured J(NO$_2$), and measured ozone, temperature, isoprene, and NO$_x$. OH measurements with interference (± 1σ) represented by the green line and measurements without interference (± 1σ) represented by the black line. For clarity, OH data shown are 2 hour averages. HO$_2$* data are 30 s averages every 30 minutes. The daily RACM2-LIM1 and MCM 3.3.1 model results for the periods when NO was measured simultaneously are also shown.

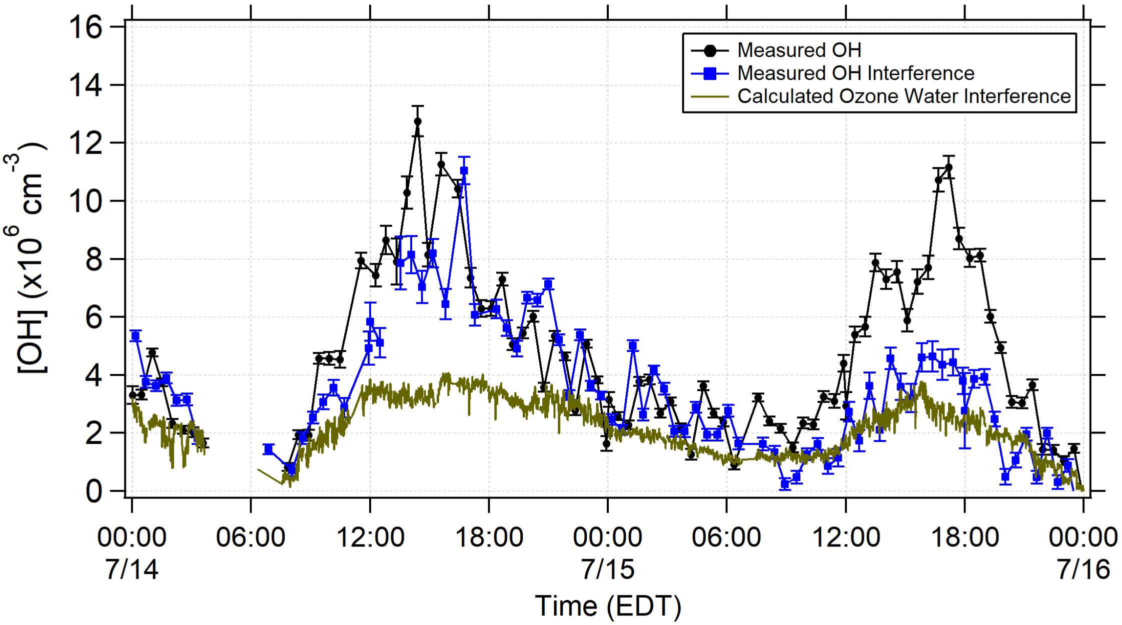

Figure 3. Averaged measured total OH signal using spectral modulation (black), and the measured interference using chemical modulation (blue) during July 14 and July 15. The calculated laser-generated interference from ozone photolysis for these days (reactions 1 and 2, green points) is also shown.

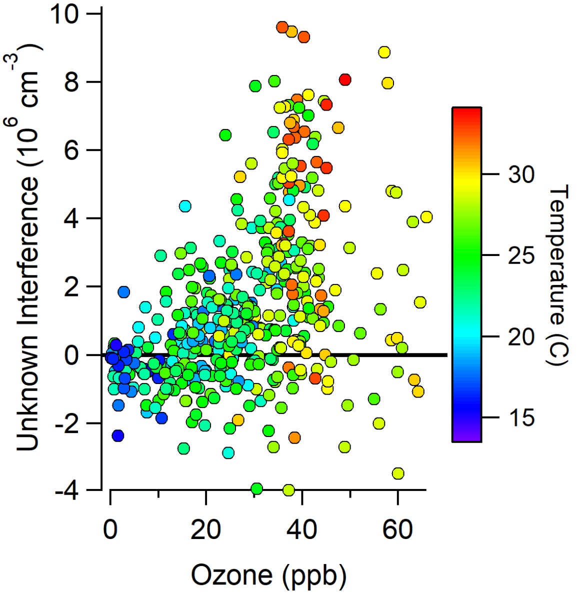

Figure 4. Measurements of the unknown interference as a function of ozone and temperature during the campaign.

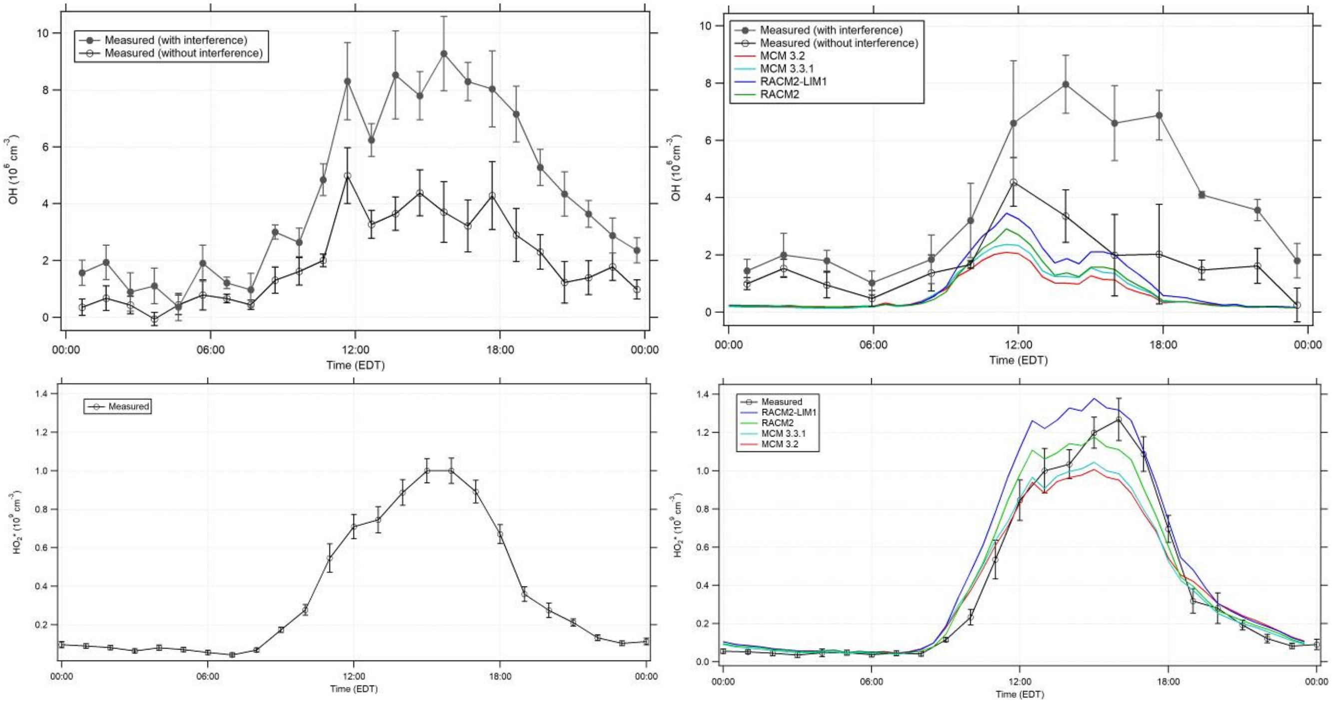

Figure 5. Diurnal profiles of OH (top) and HO2* (bottom) with the RACM2, RACM2-LIM1, MCM 3.2, and MCM 3.3.1 model results. Left panels illustrate the average of all measurements, while the right panels illustrate the average measurements when NO was measured simultaneously. The open circles represent the 1 or 2 hour mean ± 1σ standard error of OH and HO2* measurements. The filled circles represent the 1 hour mean ± 1σ standard error of the OH measurements with the interference.

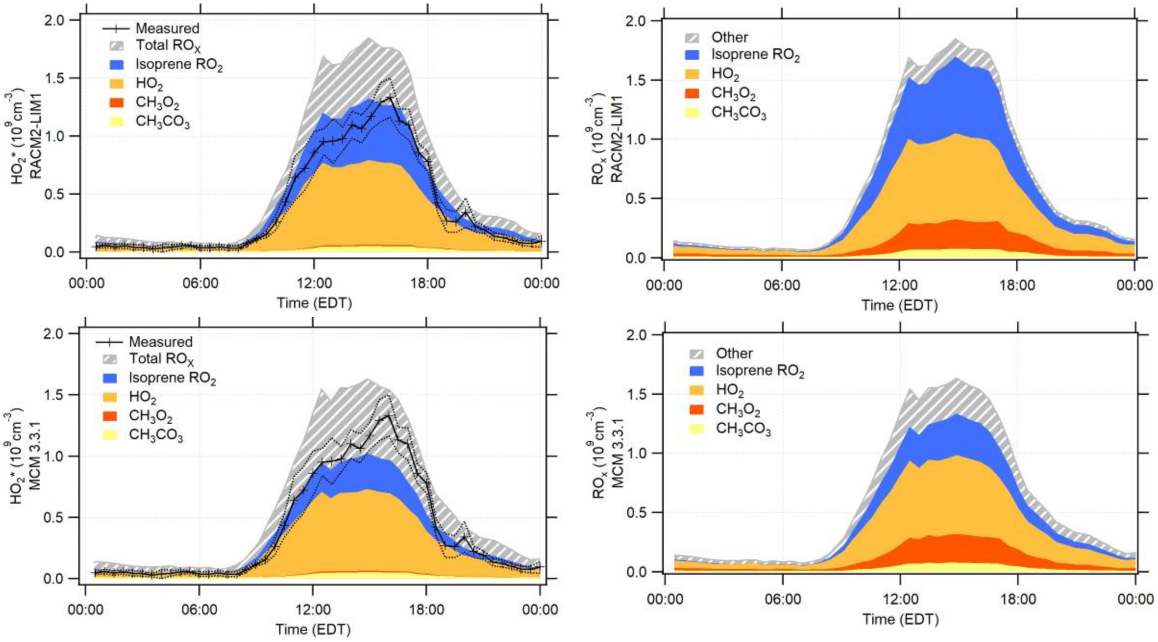

Figure 6. The RACM2-LIM1, and MCM 3.3.1 diurnal average modeled peroxy radical concentration and composition. Left panels show the modeled contribution to the HO_2* concentrations. The measured 30-min mean HO_2* concentrations are shown by the black line with ± 1σ standard error of the measurements shown by the dotted lines. The calibration uncertainty of the measurements (not shown) is 38% (2σ). Right panels show the total RO_x (RO_2 +HO_2) composition predicted by each model.

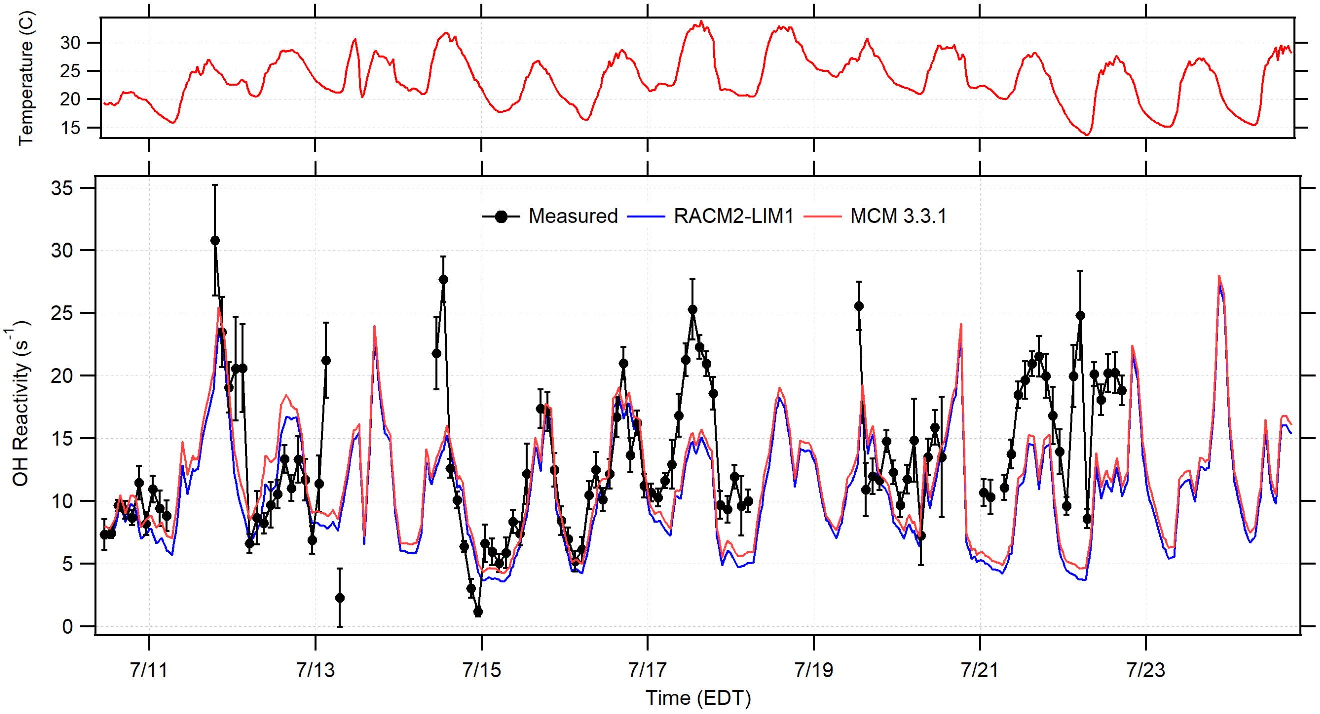

Figure 7. Time series of the 2 hour averaged OH reactivity measurements (black circles) in comparison to the RACM2-LIM1 and MCM 3.3.1 calculated OH reactivity based on measured OH sinks along with ambient temperature (top). Error bars represent the standard error of the average measurement.

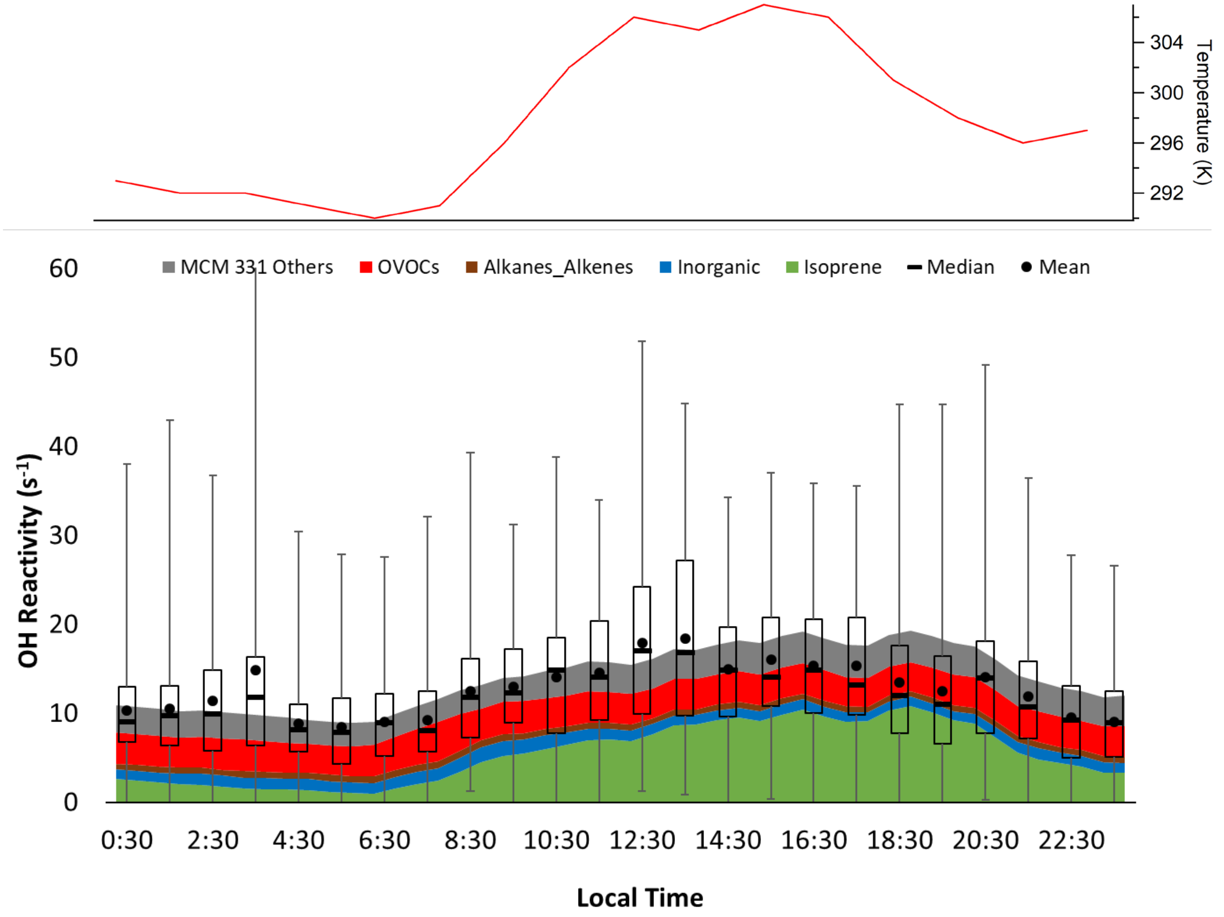

Figure 8. Diurnal temperature (top) and box and whiskers plot of observed total OH reactivity showing the mean and median values for each hour, with the mean calculated values from the measured OH sinks as well as the unmeasured oxidation products from the MCM 3.3.1 model results (Others). Error bars show the range of individual 5-min measurements and bars show Q1 and Q3 for the measured OH reactivity.

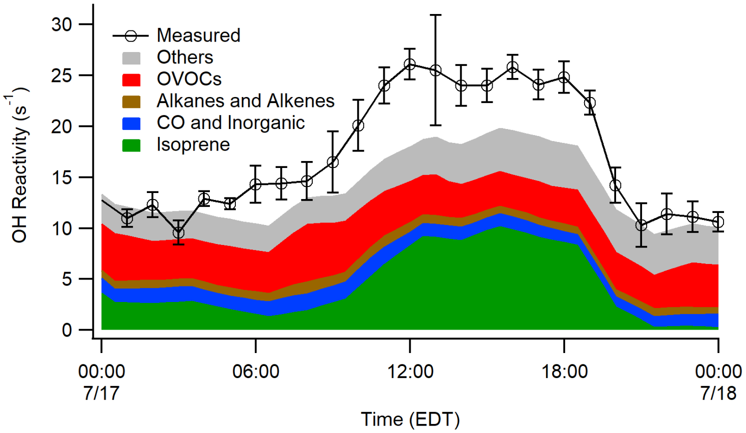

Figure 9. Median diurnally averaged OH reactivity from July 17 in comparison to modeled reactivity from the MCM 3.3.1 mechanism.

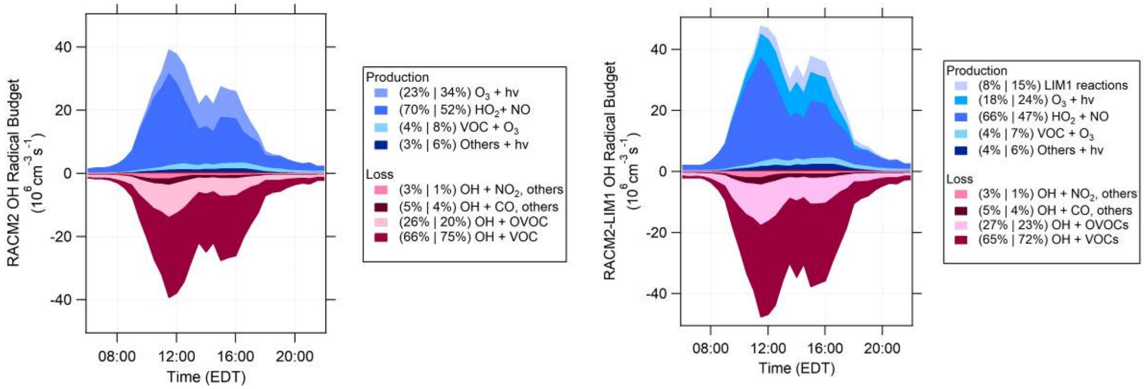

Figure 10. RACM2 (left) and RACM2-LIM1 (right) OH radical budgets for the days with NO measurements. Shades of blue represent production reactions and the shades of red represent loss rates. The percent contribution of each reaction to total production/loss are divided into two periods (10:00 to 14:00 and 14:00 to 18:00).

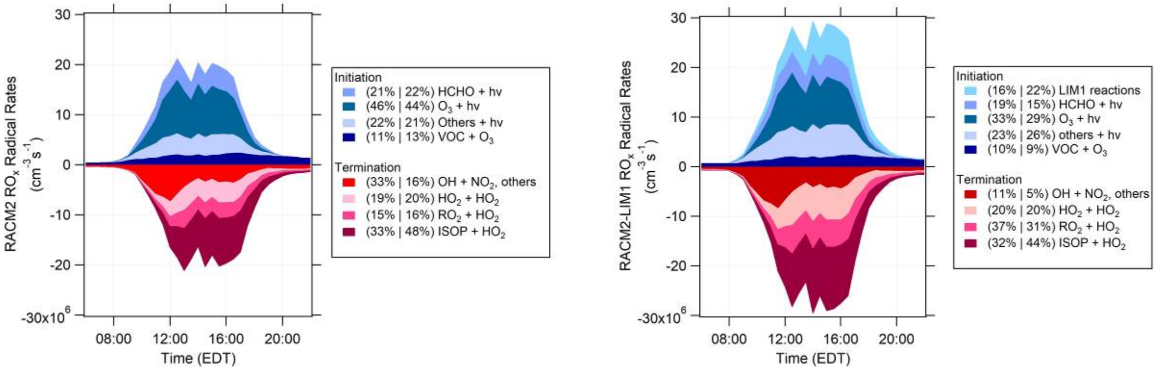

Figure 11. RACM2 (left) and RACM2-LIM1 (right) total RO_x radical budgets for the days with NO measurements. Shades of blue represent initiation rates and the shades of red represent termination rates. The percent contribution of each reaction to total initiation/termination are divided into two periods (10:00 to 14:00 and 14:00 to 18:00).