

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

Reviewer #2

The paper describes measurements of OH reactivity, OH and HO₂* in a biogenic dominated regime with medium NO concentrations during daytime in the order of a few hundred pptv and compares the measurements with a box model study using four different model schemes. The main findings are that the model describes well the measured HO₂* but underestimates the OH concentration. The most likely reason identified is a poor quality of the available NO measurements for the time period shown. When the model is constrained by NO₂ to calculate the NO concentration a better agreement of the model is found but local NO sources, independent of the photolysis of NO₂ worsen the agreement as soon as the steady state assumption cannot be made anymore. The paper also shows that the Indiana instrument successfully implemented a chemical scavenging modulation, improving the quality of the OH measurements. The quality of the dataset does not allow a detailed investigation of testing different model schemes, though it is obvious that the LIM1 based recycling reactions do provide a better agreement in the late afternoon when Isoprene is larger. The paper is well written, hPa seems to me preferable than Torr. The paper can be published after minor corrections.

P3 L11 : The statement “The extent of RO₂ radical contributions during HO₂ measurements in previous campaigns is unclear.” Is not correct. For HUMPPA 2010 the contribution of a RO₂ interference to the HO₂* signal had been estimated based on H₂O₂ in Hens et al 2014, as well as calculated based on the PAA-PAN-HO₂ system in Crowley et al. 2018 . Mallik et al. 2017 did model the internal production of OH from RO₂ as well as compared it with a NO titration scheme done routinely in ambient air during the CYPHEX 2014 campaign.

We have clarified on page 3 of the revised manuscript that while there are several campaigns where the extent of any RO₂ interference on the HO₂ measurements has been estimated and accounted for (and have included the noted references in the revised manuscript), there are many previous studies which the contribution of a RO₂ interference in the HO₂ measurements is not known:

“The degree to which the RO₂ species can interfere with HO₂ 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 RO₂ radical contributions during HO₂ measurements in many of the campaigns mentioned above is unclear.”

P4 L29 : To what extent is double pulsing an issue, considering the volume flow, the expansion of the UV beam due to the white cell and the 10kHz repetition rate?

The instrument design and configuration is similar to that described in Stevens et al. (1994). The flow velocity in the region of the White cell is likely greater than the 50 m s⁻¹ required to prevent double-pulsing of the air stream. However, any laser-generated OH is measured and accounted for through the interference measurements.

P4 L29 : please use SI units

We have converted to SI units as requested.

P6 L28 : Unclear why the precision of the HO₂* measurements is unrelated to the RO₂ interference. Why would not the variability in the relative RO₂ & HO₂ composition translate into a variability in HO₂* and therefore in an apparent precision?

We have clarified on page 7 of the revised manuscript that the instrumental precision of the measurements is primarily related to the variation in the background signal due to laser scatter and detector noise in the detection cell:

“The instrumental precision for the HO₂ measurement based on the variability of the background signal due to laser scatter and detector noise results in a limit of detection for HO₂* during this campaign of $7 \times 10^7 \text{ cm}^{-3}$ for a 30 second average (S/N =1).”*

P8 L18: Please be more specific why a constant scaling factor can be used. Hansen et al. 2014 does not describe further the reason for the factor 1.4 beyond speculating about incomplete mixing or issues with the flow speed. Without knowing the fundamental reason for the factor, the application of such seems to be arbitrary.

The constant scaling factor is derived from reproducible OH reactivity measurements in the laboratory of a variety of compounds, including butane, isoprene, and propane, which were all found to be a factor of 1.4 lower than the calculated reactivity. This has been clarified on page 8 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 (Hansen et al, 2014).”

P9 L27: Not conclusive is a 50% contribution of the background signal between 8:00 and 20:00. In the figure it seems rather in the range of 20%-300% even just for noontime. In any case I am not sure if the fractional description is of much use anyhow as the relationship between ambient OH and chemical background OH is not clear at best. I would drop the discussion about the

fractional contribution. You mention it above already that you are using a chemical scavenger method to remove ambient OH for quantification of the non-ambient OH.

We have removed this discussion as suggested.

P10 L5: Do you observe a correlation of the internal background signal with O₃*BVOC as described in Novelli 2017?

The unknown interference was found to increase with the product of ozone and BVOC concentrations, similar to that found in Novelli et al., 2017, although the correlation was not statistically significant. This has been clarified on page 10 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 not statistically significant.”

P10 L12: Novelli 2014 proposed the presence sCI decomposition as reason for the internal OH.

We have added this reference as suggested.

P11 L4: What is the time periode used for calculating the average? Did you model the non averaged time series and then average the model together with the measurements?

For the diurnal average shown in Fig. 6, the 15-min OH measurements with and without the interference were averaged into 1 hour bins. This has been clarified in the revised manuscript. The model results in this figure represent a model constrained by the diurnal average of the daily measurement shown in in Fig. 2, and is similar to the diurnal average of the model results. However, we did find a discrepancy in the model results previously illustrated in Figure 6. This has been corrected in the revised manuscript, and all the relevant figures have been updated.

P11 L14: “However, as seen in Fig. 6, . . .” sentence seems to be reduntant to “If the measured interference was not subtracted from the total OH. . .“

We have removed this sentence as suggested.

P11 L27: Is there a NO source close by and to what extend is the assumption of steady state NO/NO₂ justified? The floating NO leads to much better model estimates for OH, but seems to deviate as soon as the sun sets. From a model point of view, NO production in the model will follow JNO₂, which decay quickly into the night and reduce the OH source from HO₂+NO

whereas the measured OH is significant different from 0, therefore the question, is there a still active NO source close by?

As pointed out by the reviewer, the models tend to underpredict the measured nighttime NO, suggesting that the site may be influenced by transportation by the nearby highway or perhaps more importantly local emissions of NO from soil. These active NO source likely impact the measured OH concentration and could explain the discrepancy between the measured and modeled OH concentrations in the late afternoon and early evening. This has been clarified on page 12 of the revised manuscript:

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

P11 & P16 Check spelling of the name, Rohrer

This typo has been corrected.

P 16 L25: Mallik et al, 2017 like Mao found a decent agreement of modeled OH and measured OH only when the interference, determined by a chemical modulation technique had been taken into account. I would be careful with a generalization, the instrument by the Leeds and Juelich group seem to be not as much as sensitive to the interference as the PennState/Indiana/Mainz & Lile group. The most striking difference is the use of a multipass cell vs. single beam cell.

We have included the Mallik et al., 2017 reference as suggested. We agree that the observed interference may not be similar for all instruments, and have revised the statement accordingly on page 17 of the revised manuscript:

“However, it is clear that if the measured interference was not taken into account, the apparent OH concentrations would have been a factor of 5 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. However, 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.”