Response to RC1

This manuscript describes OH interference measurements performed using the Leeds LIF FAGE instrument with the inclusion of an inlet pre-injector during three separate field deployments. I was very interested in reviewing this manuscript due to its importance in the measurement of ambient OH. With large reported discrepancies between measured and modeled OH and the significance of accurate OH measurements, it is important for all LIF groups to conduct these tests. This manuscript is thorough and well written; however, I have concerns regarding some of the analyses which I believe can be resolved with further clarification. Nevertheless, once these changes are made, I fully recommend publication in AMT.

We thank the reviewer for their kind comments. Below we present the comments of the reviewer (blue text), then our responses to individual comments and changes made in the revised manuscript (black text).

Specific comments

Figure 5: Do the authors have any thoughts on why there is more variability in the propane results? And why does C3F6 produce a more gradual decay?

Some of the propane results were collected when the FAGE instrument was operating with a higher background than usual, leading to more scatter in the data. Considering we are measuring on the order of <1% OH remaining, we would expect some scatter in the data. With this considered it is clear that propane and C3F6 follow the same general trend. Finally, we do not believe this affects our main point that under the IPI operating conditions used during field campaigns, >99% of ambient OH should have been scavenged away.

P11, line 367: I suggest the authors consider adding the description of the injector tip to Figure 1 for clarity. In addition, can it be clarified that this injector tip is not interrupting the sample flow?

We have added “through 1/8” stainless steel tubing” after “injected” in the revised MS. We cannot clarify that the sample flow is interrupted by the injectors and see this as a limitation to our approach for determining internal OH removal. Since the NO injector tip was only moved for the purpose of the internal removal experiment, we have chosen not to add this to Fig. 1 (in ambient HO_2 detection, NO is injected 7.5 cm below the pinhole).

P13, lines 464-71: I suggest the authors perform a simple modeling test to determine if SCIs are the likely cause of this interference. While it is negligible when extrapolated to ambient concentrations, acknowledgement and quantification of this interference, if it is in fact from SCIs, can be used in comparison with other FAGE instrumental overviews.

We agree with the reviewer that modelling the SCI decomposition and quantification of the interference would be useful for comparison to other FAGE instruments. We have added the following sentences to Section 3.2.2:

"Similarly, we have modelled the SCI decomposition in our FAGE cell. Assuming an ambient atmosphere containing 100 ppbv O_3 and 10 ppbv alkene and taking the reactions and rate coefficients from Novelli et al. (2014a), we calculate an equivalent ambient pressure OH concentration of ~4×10^3 molecule cm^{-3} from the decomposition of SCIs at our FAGE cell residence time of 2 ms."

Novelli, A., Vereecken, L., Lelieveld, J., and Harder, H.: Direct observation of OH formation from stabilised Criegee intermediates, Phys. Chem. Chem. Phys., 16, 19941–19951, 2014.

Figure 10: Do the authors have any suggestions as to why there appears to be greater variability at lower OHwave and OHchem measurements? Assuming the majority of these points are nighttime measurements, is NO3 responsible? Overcorrection of O3/H2O?

We suggest the perceived greater variability at low OH is simply due to more datapoints being collected at low OH, thus making it more likely to see outliers. NO_3 interferences have been ruled out as insignificant in laboratory tests, and we believe the O_3/H_2O interference has been well quantified, although since this is very small it is difficult to measure accurately.

Section 2.3: More information about the field deployments needs to be presented. How long (#days) were each deployment? Were measurements continuous?

The text has been modified accordingly.

ICOZA: "Two continuous IPI sampling periods were conducted in the middle of the campaign, separated by a few days (3rd–8th July and 12th–16th July), with a total of nine days where OHchem measurements are available around midday. For other times, only measurements of OHwave are available. During the IPI sampling periods, power cuts on the nights of 3rd/4th July and 6th/7th July resulted in data loss."

AIRPRO: "In winter, OHwave and OHchem were measured simultaneously for 6 days of the campaign. In summer, almost one month of near-continuous IPI data are available, with one day of interruptions due to IPI testing (see Section 3.1.2)."

The authors later mention instrumental issues such as power outages. This would be the section to provide more detail about such matters.

We have added the following sentence to the text referring to ICOZA: “During the IPI sampling periods, power cuts on the nights of 3rd/4th July and 6th/7th July resulted in data loss.”

P 16, lines 544-8: Did the authors compare OHint to the same parameters that were previously implicated? It seems that since there was little to no OH interference measured, that by comparing OHwave and OHchem individually to these parameters, the trend will largely be representative of actual OH.

We agree with this comment and have looked at correlations of OHint with other species. For ICOZA, no dependences were found on parameters previously implicated:

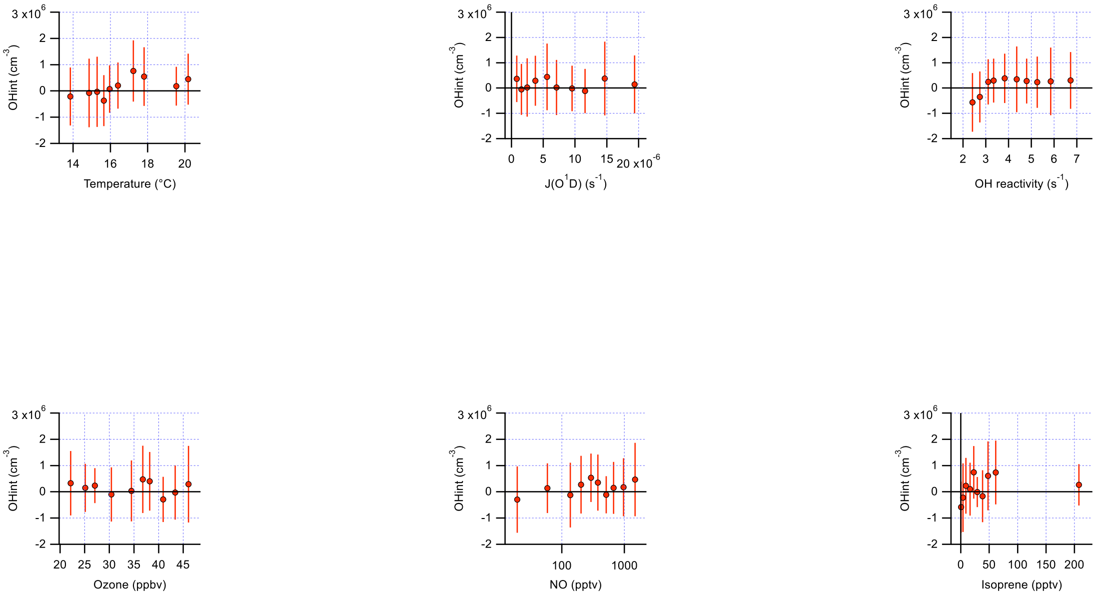

Figure 1. Daytime ($J(O^1D) > 5e-7$) OHint binned against various parameters for the ICOZA campaign. Error bars correspond to 1 SD.

The case was similar for AIRPRO summer:

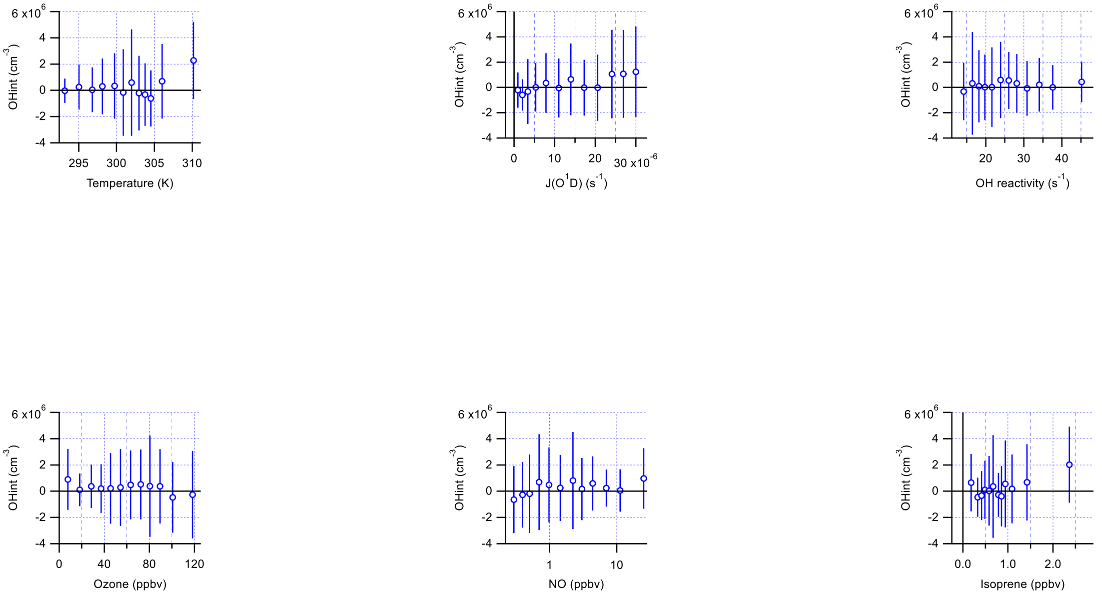

Figure 2. Daytime (J(O^{1}D) > 5e-7) OHint binned against various parameters for the summer AIRPRO campaign. Error bars correspond to 1 SD.

Although, it can be seen that OHint was marginally higher in the highest temperature, JO1D, and isoprene bins. We have decided to included these figures in a supplementary information file, and referenced them in the main MS.

P16, lines 558-9: Are the authors convinced that an over-subtraction of O3/H2O is not occurring during the daytime as well? Figure 13 shows OHchem larger than OHwave at peak concentrations. In addition, AIRPRO summer 2017 reports a negative interference ratio (-0.09). Is this also related to an over correction of O3/H2O? The authors are encouraged to give more insight into this.

We believe the O3/H2O interference has been well quantified, although since this is very small it is difficult to measure accurately (see, e.g., the high scatter in Figure 7). The scaling factor in equation (E7) has a 2σ uncertainty of 140 molecule cm^{-3} ppbv^{-1} %$^{-1}$ mW^{-1}. Subtracting this from the actual factor (520 molecule cm^{-3} ppbv^{-1} %$^{-1}$ mW^{-1}) yields a lower limit for the O3/H2O interference. Below shows the effect of using this lower limit interference to correct OHwave data, resulting in less negative OHint. However, in both the original and lower limit cases, OHint is still more negative than the 1 h LOD in the afternoon. OHint levels less negative than the 1 h LOD can only be achieved by reducing the O3/H2O interference to zero. It is not clear why this is the case. Since the O3/H2O had to be determined at very high O3, one possibility is that, in our instrument, the dependence is nonlinear at ambient O3 levels.

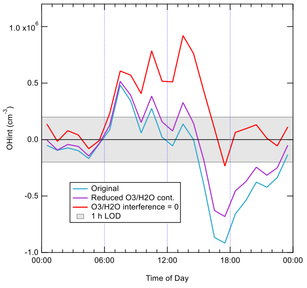

Figure 3. Effect of reducing the known interference from O3/H2O.

P16, line 573: Do the authors have any suggestions for why the nighttime OH levels were so much higher during AIRPRO summer 2017 in comparison to the other two campaigns?

Interpretation of the chemistry is beyond the scope of this work but will be discussed in detail in forthcoming manuscripts. It is likely that the AIRPRO summer campaign had much more active NO_3 and ozonolysis chemistry due to high nighttime NO_2, O_3, and NO_3, leading to increased nighttime radical production. In other field campaigns in China, significant nighttime OH concentrations have also been found. For example, in Lu et al. (2014), nighttime OH was up to 3×10^{6} molecule cm^{-3}, which is higher than the nighttime OH in our work. To reconcile such high OH levels required the inclusion of additional RO_x production processes in their model.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Brauers, T., Oebel, A., Dlugi, R., Hu, M., Li, X., Lou, S. R., Shao, M., Zhu, T., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Nighttime observation and chemistry of HO_x in the Pearl River Delta and Beijing in summer 2006, Atmos. Chem. Phys., 14, 4979–4999, https://doi.org/10.5194/acp-14-4979-2014, 2014.

P17, line 578-87: While there are few points of high OH measurements, was any analysis performed on their relationship with BVOCs, O3, or temperature? Were these high concentrations measured on different days/times? While it may be limited, the authors are suggested to provide more of an analysis of these points.

Please see our relevant response above. For AIRPRO summer, no clear dependence of OHint was found on isoprene, O_3, or temperature.

P18, lines 611-13: The sentence ‘These findings. . .in this type of environment.’ should be reworded or omitted. While one of the field sites showed high BVOC and low NO concentrations, it should not be implied as being representative of a forested environment. While the BVOC and NO conditions may have been similar, other key compounds, such as SO2, would have likely been larger, altering the environmental conditions further from that of a forest.

We have reworded the sentence to: “Although AIRPRO summer took place in a city, its results do provide confidence in previous measurements of OH using the same instrument, and support the hypothesis that there are unknown OH sources in the atmosphere.”

Technical corrections

Abstract. P1, line 21: change scavenging to scavenger

Done

P3, line 81: either remove the word ‘by’ or change to ‘Mao et al. (2012)’

Done

P3, line 82: Lew et al., 2019 should be added as a reference for OH interference measurements in a forested environment

Done

P5, line 175: add reference Rickly and Stevens, 2018

Done

P8, line 267: move comma to read as ‘AIRPRO winter, but after’

Done

Figure 4: make red and blue markers consistent with graph 3

Done

P9, line 303: remove second ‘reduction’ in this sentence

Done

P12, line 398: change to ‘OH removal efficiency of ∼12%’

Done

P16, line 567: change ‘as’ to ‘because’

Done

P17, line 590: either remove ‘of’ or change to ‘Fittschen et al. (2019)’

Done

P17, lines 599-601: The authors are suggested to add ‘in moderately to highly polluted environments’ to the end of this sentence for clarification.

The sentence has been changed to: “The results from the three field campaigns that feature in this work demonstrate that, in moderately to highly polluted conditions, the Leeds ground-based FAGE instrument does not suffer from substantial interferences in the measurement of OH using the conventional, wavelength-modulation background technique, OHwave.”