

Response to Anonymous Referee #1

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.

I was very interested to review this manuscript which falls well within the scope of AMT and reports on the extremely important subject of potential OH artefacts in LIF instruments used for ambient OH measurements. Although other LIF groups have reported their findings from their own LIF instruments (Mao et al, Novelli et al and Fuchs et al), it is very important for the experiments presented in this manuscript to be conducted and published by every LIF group involved in ambient OH detection. In this manuscript there are a few key experimental details missing in places, particularly the Inlet Pre Injector parameters, which need to be included in the revised manuscript (discussed below). I also have some concerns over the experimental approach (which will likely be resolved once further experimental detail is provided) and the presentation of the results could be improved upon. Notwithstanding, once these changes are made I fully recommend publication in AMT.

Specific comments

Abstract: In general there needs to be further specific details on the key findings included in the abstract.

Line 16: 'several BVOCs..' these should be named in here

We have added the names of each of the BVOCs measured to the abstract as suggested.

Line 18: 'an interference under high ozone and BVOC concentrations was observed..' It is important to state the level of the interference in the abstract. I understand that this level varied with [O₃] and [BVOC] and BVOC type, but I suggest reporting the maximum interference observed and giving the concentration of the pre-cursors for a particular experiment. It is also important to state here the anticipated interference under ambient conditions somewhere in the abstract.

As suggested, we have added the average level of the interference observed and the range of precursor concentrations to the abstract. We have also added a statement concerning the anticipated interference under ambient conditions.

Pg 2, lines 28-30: Mention specific chemical condition under which the measurements were made.

We have added that the measurements were made under varying concentrations of H₂O, O₃, CO, HCHO, NO, and NO₂ as described in Schlosser et al., 2007.

Pg 4, lines 10-11: What is the motivation for choosing these specific BVOCs? Has ocimene been observed at appreciable levels in forested environments?

The BVOCs chosen represent major monoterpene emissions (α - and β -pinene) as well as a frequent emission (cis-ocimene) (Guenther et al., Atmos. Environ., 28, 1197-1210, 1994), in addition to isoprene and MBO. This has been clarified.

Pg 5, line 2: Although no OH or artefact signal was observed during experiments conducted with isoprene and MBO, the experimental conditions, i.e. the concentration of isoprene and MBO (and ozone concentration if different from the other ozonolysis experiments) should be added to the experimental section.

We have added the approximate concentrations of both isoprene and MBO used in these experiments to the experimental section as suggested.

Section 2.1: It is unclear which laser was used for the experiments detailed in this manuscript.

This has been clarified in the revised manuscript.

How do the pressures tested in these experiments compare to those typically employed during ambient measurements?

We have clarified the normal operating pressures and inlet lengths typically used during previous ambient measurements as suggested.

Section 2.2: The authors need to provide additional details on their chemical titration scheme. Specifically, what is the total flow rate through the chemical titration section of the instrument? What is the concentration of C₃F₆ added (in molecule cm⁻³)? What is the residence time of gas in the chemical titration section? These parameters are important as I worry that if only 90% of a point OH source (from the calibration wand) is removed by the scavenger, then even less OH generated via a steady state source (O₃+BVOC) will be removed and this could lead to a bigger percentage of the OH signal observed being assigned as an interference than is necessarily the case. Other experimental results presented, such as the agreement of the OH yield with literature values, and the variation in the magnitude of the interference with inlet length do suggest that the amount of scavenger injected is sufficient to remove a steady state source of OH, but it is important to demonstrate this absolutely. The authors could consider presenting results from a simple kinetic model which includes the main OH source (O₃+alkene) and sink reactions (OH+alkene, OH+C₃F₆ reaction), run over the residence time in the chemical titration section, to demonstrate this?

We have expanded the description of the chemical titration scheme in this section, including a schematic diagram of the injector ring in Figure 2. We have also included estimates of the concentration of C₃F₆ added and the residence time in the titration region as suggested. We have also provided results of a simple kinetic model, which shows that the amount of C₃F₆ added and the residence time in the titration region, is enough to reduce the steady-state concentration of OH from the ozonolysis reactions to below the detection limit of the instrument for the majority of the experiments described here. However, it is possible that for some of the high concentration experiments, the amount of C₃F₆ added may not have been sufficient to reduce the steady-state concentration of OH to below the detection limit, especially for the ocimene experiments due to the high reactivity of ocimene with ozone. However, the model simulations suggest that even for these high concentration experiments the remaining steady-state OH concentrations represented less than 10% of the observed interference. This has been clarified in the revised manuscript.

Pg 8, lines 27, 28: There does seem to be some trend with beta-pinene concentration?

We have added a statement indicating that there appears to be a trend in the measured OH yield with increasing β -pinene concentration.

Pg 9, line 15: As well as reflecting the 'higher reactivity' of the mono-terpenes with ozone compared to isoprene and MBO, important also (to the real OH signal) is relative reactivity of BVOC+O₃ vs BVOC+OH (and the OH yield from ozonolysis). All should be mentioned as possible reasons for the lack of real OH signal observed. I am a little surprised that no OH signal was observed during these experiments even with the shortest inlet given the limit of detection stated in section 2.1.

We have clarified that the lower expected steady-state OH concentration in the ozonolysis of isoprene and MBO are lower due to the relative reactivity with ozone and OH as well as the overall OH yield as suggested. We have also performed simulations that show that the expected OH concentration in the isoprene experiments were approximately 50 times lower than that for the α -pinene experiments, consistent with a lower steady-state OH concentration estimated using Equation 1, and near or below the detection limit of the instrument.

Is the concentration of SCI in the isoprene+O₃ and MBO+O₃ experiments estimated to be lower than during the monoterpene+O₃ experiments? The rate coefficients, k_{isop+o_3} and $k_{betapinene+o_3}$ are similar.

As pointed out by the reviewer, simulations using the Master Chemical Mechanism suggest that the concentration of SCIs in the isoprene + O₃ experiments is similar to that in the α -pinene + O₃ experiments. This may suggest that a similar interference should have been observed during the isoprene experiments as was observed during the α -pinene experiments. Given that OH yield from the decomposition of excited CIs in the isoprene mechanism is lower than that for the α -pinene mechanism, the absence of a detectable interference in the isoprene experiments described here may suggest that the decomposition of these intermediates inside the FAGE detection cell may also be slower. As a result, the observed interference for each alkene is likely proportional to the OH yield from the ozonolysis mechanism. This is consistent with the observation that the observed interference appears to be a constant fraction of the total OH yield in these experiments independent of the ozone concentration and the turnover rate (Figs. S5 and S6). This has been clarified in Section 3.3 of the revised manuscript.

Pg 10, lines 27- 30: It is interesting/perplexing that the artefact signal is actually lower when the medium inlet is used than when the shorter inlet is used. In light of previous results (Fuchs et al. 2016) which demonstrated a dependence of the magnitude of the artefact signal on cell residence time a comment on the lack of trend in level of interference and inlet length is needed here.

As pointed out by the reviewer, the level of the observed interference is similar for the short and medium length inlet, but increases with the longest inlet. This suggests that the level of interference is not directly related to the residence time inside the FAGE detection cell, but may be the result of increased collisions with the interior surfaces of the detection cell that occurs when using the longest inlet. We have clarified this here, as well as in the previous discussion in Section 3.1.

Section 3.3: The working hypothesis on the identity of the observed OH interference is that it derives from the decomposition of a SCI. Were any experiments conducted with alkene concentration in excess? Under these conditions the concentration of the SCI would be maximised, whilst the concentration of externally generated OH from ozonolysis would be small, meaning that the artefact signal should be readily distinguishable from a real OH signal?

Unfortunately, due to the low vapor pressures of these compounds we were unable to generate high enough concentrations of the alkenes to conduct experiments with them in excess.

Pg 12, lines 1 – 17: What was the concentration of acetic acid added to the flow-tube? Would any loss of OHs by reaction with acetic acid be expected given the residence time?

For these experiments, approximately 9×10^{12} molecules cm^3 of acetic acid was introduced into the flow tube and allowed to react for approximately 200 ms. At this concentration, the reaction with acetic acid was modeled to have a minimal impact on the steady-state concentration of OH, as the rate constant for the OH reaction is approximately $7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This has been clarified in the revised manuscript.

Pg 12, lines 22 – 24: 'Based on these results, the observed OH interference in these experiments could be explained if approximately 5% of these intermediates dissociated.. 'Does this then effectively disprove the hypothesis that the transmission efficiency of SCI vs OH through the pinhole is substantially different? A comment on transmission efficiency assumed for these lab results vs transmission efficiency estimated from field results (and the implications of these differences) would be welcomed in the revised manuscript.

It's not clear whether the results of these experiments and modeling disproves the hypothesis that the transmission efficiency of SCIs are substantially different than that for OH, as it is possible that the transmission efficiency of SCIs through the inlet is high, but only 5% of those entering the detection cell actually dissociate into OH.

In these experiments, as well as in field studies, we are assuming that the transmission efficiency of SCIs is essentially 100% and similar to the transmission efficiency of OH. This is based on previous measurements of the loss of OH on different inlet designs and coatings on a similar LIF instrument inlet, as well as measurements of the calibration factor with and without the inlet, suggest that heterogeneous loss of OH on the inlet is minimal (Stevens et al., 1994). This has been clarified in Section 3.3 of the revised manuscript.

Technical corrections

Pg 2, line 26: 'their' to 'Penn State'

Added as suggested

Pg 4, line 15: add ' with sliding injector' after 'flow tube' so the later discussion on the injector is easier to follow.

Added as suggested.

Pg 4, line 17: Define 'IU-FAGE'

Defined as suggested.

Pg 6, line 20: add ' compared to chemical modulation' after 'spectral modulation'?

Added as suggested

Pg 6, line 21: change 'reflect' to 'can reveal'?

Changed as suggested.

Pg 6, line 25: is this 3 – 5 sccm of 1% C₃F₆ in N₂ or 3 – 5 sccm pure C₃F₆?

This has been clarified as 3-5 sccm of 99.5% C₃F₆.

Pg 9, line 7: ± 0.9 is a very large error. Is this correct?

The actual error is ± 0.09 and has been corrected.

Pg 10, line 19: Define ‘turnover time’

We have defined the turnover time as the steady-state rate of OH radical propagation, expressed as the alkene ozonolysis rate.

Figures: Stick to [O₃] in molecule cm⁻³ or ppm.

We have converted all graphs to concentration units, as suggested.

Figure 3 – 7: Axes should be rescaled and legends should be made more self-explanatory. It took me a while to understand what ‘Pcell 4’ actually represented.

We have rescaled the graphs and have clarified the legends to make them more self-explanatory, as suggested.

Figure 3 & 4: It isn’t clear to me why the OH yield from the ozonolysis reactions and the OH signal without scavenger are on the same graph? They are two distinct results that just happened to have been determined in the same experiment. I am struggling to suggest a better way to present the results, but maybe the authors could critically review these figures before final publication?

We included the OH yield from the ozonolysis reactions with the measured OH signal without the C₃F₆ scavenger to illustrate the magnitude of the measured interference. We have clarified this reasoning in section 3.1 of the revised manuscript.

Figure 4: Include a legend on this figure that clearly states the VOC concentration for the different experiments, e.g. green = x cm⁻³

We have modified the legend to include the VOC concentrations for each experiment as suggested.

Figure 5: it is not obvious to me why these three panels are grouped together? The recommendations for improving the figures above should be considered for the figures included in SI also.

We have grouped the panels in Figure 5 together for simplicity, similar to Figure 6 in Fuchs et al., 2016. We have also changed the figures in the Supporting Information, as suggested.