

Interactive comment on “Measurements of the OH radical yield from the ozonolysis of biogenic alkenes: A potential interference with laser-induced fluorescence measurements of ambient OH” by Pamela Rickly and Philip S. Stevens

Anonymous Referee #1

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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

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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

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.

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

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

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.

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

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

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?

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

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+o3} and k_{betapinene+o3} are similar.

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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.

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?

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?

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.

Technical corrections

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

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

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

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

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

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

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

Pg 10, line 19: Define 'turnover time'

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

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.

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?

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

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.

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