

Interactive comment on “Measurement of OH reactivity by laser flash photolysis coupled with laser-induced fluorescence spectroscopy” by Daniel Stone et al.

Anonymous Referee #3

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There are currently 3 techniques used in the field to measure Total OH reactivity and this manuscript describes one of these techniques, which is based on Laser Flash Photolysis- Laser Induced Fluorescence (LFP-LIF). The authors provide a description of their instrument and discuss the attempt to use two different coupling setups between the sampling reactor and the LIF detection of OH (sampling along or at 90° of the air flow direction). Details are given about zeroing the instrument, which is a critical aspect of LFP-LIF instruments. Examples of measurements made in an atmospheric chamber and in the atmosphere are also reported to illustrate the performances of this new instrument.

This manuscript is clear and well structured, and will be of interest for the atmospheric

C1

community. However, since this is an instrument paper, I recommend to add additional details about operating conditions and analytical figures of merit (see my comments below). I therefore recommend publication in ACP after the authors address the following comments:

Abstract: Please provide figures of merit in the abstract (limit of detection, precision, total uncertainty).

P1 L38-39: You could also mention that when a disagreement is observed between measured and model-calculated OH concentrations, it is not straightforward to determine whether this is the loss rate of OH that is miscalculated by the model or the production rate.

P2 L63: I would replace “mixing time of OH with the ambient air” by either “contact time of OH with the ambient air” as written on L73 or “reaction time of OH with ambient trace gases”. Once OH is well mixed in the air flow, it is not a mixing time anymore.

P3 L86-87: Please provide references for CRM instruments incorporating PTRMS, GC-MS and GC-PID detectors.

P3 L95: It is mentioned that the correction to apply on the CRM measurements requires knowledge of HO₂ and NO. It is wrong. Only NO is needed.

P3 L100: “. . . produces OH in isolation via . . .”. The formulation is not clear. Please reword.

P5 Eq.4: Is this equation needed? This is common knowledge. I would suggest to remove this equation and to indicate in the main text the upper limit of Re to get a laminar flow regime.

P5 L195-199: Please indicate the repetition rate of the pump laser? Is the sampling cell refreshed between each laser pulse? If not, how can it impact the OH reactivity measurements?

C2

P5 L210: "... sufficient production of OH ..." Please indicate the range of OH concentrations produced in the sampling reactor under ambient conditions?

P5 L213-215: Since a mercury lamp is used to produce O₃ in a small flow of humid air OH and HO₂ radicals will also be produced from water photolysis at 185 nm. Could a significant amount of H₂O₂ be produced from OH+OH and HO₂+HO₂ reactions before the air flow reaches the sampling reactor? and as a consequence could a significant OH reactivity be generated from OH+H₂O₂?

P6 L232-233: "... air that has not experienced the photolysis laser (containing only ambient OH concentrations) ..." Can OH really make it through the sampling line?

P8 L349-P10 L353: Please indicate the range of water concentrations used for calibration. It is mentioned that 1E9 cm⁻³ of OH is produced in ambient air by the pump laser. Please also report the O₃ and water concentrations, as well as the pulse energy leading to this initial OH concentration. What is the range of initial OH concentrations observed during field measurements? How variable is it? The reported detection limit is approximately 1E7 cm⁻³. The signal-to-noise ratio used to calculate the detection limit and the integration time should also be reported.

P9 L380-381: It is mentioned that errors in k_{phys} and f are factored in the measurement uncertainty. Please report the relative magnitude of these errors.

P9 L389-390: What were the main species quantified in the zero air? Concentrations? How was the zero made on the GC instrument if zero air still contains VOCs? Can you rule out that the peaks observed on the chromatogram do not come from internal contamination of the GC?

P10 L398-399: What is the precision on k_{phys}? Does the standard deviation given in the text reflect real variability of k_{phys} over time or is it close to the precision of the k_{phys} measurement?

P10 L413: Please report the ranges of CO and CH₄ concentrations as well as the

C3

ranges of OH reactivity used in these experiments. Did you do replicates at each concentration? If so, could you use these experiments to show how the measurement precision changes with the OH reactivity?

P10 L532-435: May be interesting for the reader to briefly summarize the model-measurement comparison from Whalley et al. It is mentioned that the data is shown to highlight the instrument capability. Please discuss this point? What are the figures of merit of this instrument for ambient measurements (detection limit, precision, total uncertainty)?

P11 L464-465: How does the dilution impact the measurement total uncertainty?

P12 L487-490: Please expand the discussion on this issue. Is OH lost inside the FAGE instrument through bimolecular reactions?

Figure 2: The chronogram shown for the photon counting card is not discussed in the caption neither in the main text. I would suggest removing it.

Figure 3: Why does OH increase over 15 ms after the laser pulse? Is it due to the O(1D)+H₂O kinetic? How long after the laser pulse did you choose to start the fit? Why? Caption of Figure 4: it is mentioned that error bars are 1 sigma. Is it the error from the mathematical fit only or does it include other sources of errors?

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C4