

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

Anonymous Referee #2

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This paper describes a new instrument designed to measure total OH reactivity using laser flash photolysis combined with laser-induced fluorescence (LP-LIF) detection of the OH radical. Measurements of total OH reactivity provide an important constraint to our understanding of OH radical chemistry. Comparison of measured total OH reactivity with model calculations and measurements of ambient volatile organic compounds can provide information on whether all OH radical sinks are accounted for in current models of atmospheric chemistry.

The instrument is similar in design to several previously developed instruments and the authors provide examples of measurements of OH reactivity in both an urban environment and a more rural environment, demonstrating the ability of the instrument to

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measure a wide range of OH reactivity.

The paper is well written and suitable for publication in AMT after the authors have addressed the following:

1) The authors find that measurements of OH reactivity sampling perpendicular to the flow and photolysis beam resulted in biexponential decays (similar to that observed in other LP-LIF instruments), while sampling at the end of the reactor along the axis of the flow and photolysis beam resulted in exponential decays due to the reduced impact of diffusion when sampling in the center of the flow. It would be useful to show these decays in comparison to the exponential decays. Even though the decays in the perpendicular configuration are biexponential, are the decays at long reaction time consistent with the decays measured with OH detection at the end of the reactor?

2) Do the authors consider recycling of OH due to OH + VOC reactions after OH generation? Under conditions when the mixing ratio of NO is high, the peroxy radicals from these reactions could produce OH radicals at long reaction times leading to an underestimation of the OH reactivity. Hansen et al. (Atmos. Meas. Tech., 8, 4243–4264, 2015) observed biexponential decays at long reaction times due to recycling of OH and that fitting the decay with a monoexponential can lead to a bias in the measured reactivity. Although it appears that the OH signal does go to zero in Figure 3a, have the authors observed biexponential decays at longer reaction times during polluted (high reactivity) events due to OH recycling in their instrument?

3) It's not clear from the information given in the manuscript how the authors fit the exponential decays. In the caption of Figure 3 it is stated that time zero is the time at which photolysis occurs, but on page 9 time zero for $S_{OH,0}$ is defined as “immediately following firing of the 266 nm laser and production of OH in the reaction cell.” This should be clarified in the revised manuscript. Is time zero fixed for all decay measurements? The fits shown in Figure 6 appear to begin at different times and at the max OH signal. How does the definition of time zero impact the fits?

4) The authors state that the time between entering the FAGE detection axis and detection of the fluorescence leads to an underestimation of very high reactivities. The reason for this is not explained although it appears that it will be addressed in a future publication (Stone et al., 2016). How does the sampling time in the FAGE detection cell lead to an underestimation of the reactivity? Is this the result of an interference leading to the formation of OH inside the FAGE cell, similar to that observed in other LIF-FAGE instruments (Mao et al., Atmos. Chem. Phys., 12, 8009–8020, 2012)? Or is it due to recycling of OH through peroxy radical reactions? What level of reactivity does sampling issues with the FAGE axis impact the OH reactivity measurements? Does the underestimation depend on the level of NO in the chamber? The paper would benefit with an expanded discussion of this issue.

5) There is also little discussion of potential interferences, such as the production of HO₂ from the photolysis of HCHO by the photolysis laser leading to OH recycling through reaction with NO. Although other studies have suggested that such interferences are negligible, can the authors estimate whether this (and other potential interferences) impacted their measurements during ClearLo? What mixing ratio of HCHO would lead to a significant interference given the pulse energies used for photolysis? Could photolysis of other compounds, such as carbonyl compounds, lead to interferences from peroxy radicals?

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