

We thank the reviewers for their careful reading of the manuscript and for their comments, which will improve the manuscript. The reviewers' comments are given in bold type below, followed by the responses in normal type, with additions to the manuscript given in italics.

## Review 1

The paper « Measurement of OH reactivity by laser flash photolysis coupled with laser-induced fluorescence spectroscopy » by Stone et al. describes the pump-probe instrument such as used by the University Leeds. Laser photolysis coupled to FAGE has been described first by Sadanaga et al. in 2004 and has since been used and further developed by several groups. In this context, the paper, which is well presented, provides general information and does not give a very detailed view of the specificities of the Leeds' instrument.

The paper starts with a good introduction to OH reactivity and the description of different measurement methods currently used by the scientific community. It also gives an overview of results on OH reactivity measurements obtained during field campaigns until today by different groups and techniques. In section 2, the instrument is described, as well as how the OH reactivity is obtained and validated. Finally 2 types of application of this instrument are presented: use during two field campaigns and first measurements of a coupling of this instrument with the HIRAC chamber. I think such a paper with the detailed description of this instrument, data acquisition procedure and validation is very interesting. However, all sections are kept very general and contain only little detail, this should be completed before considering publication in AMT.

Here are suggestions on what could/should be described in more detail:

- I'm not sure if it is necessary to show the set-up in configuration with the reaction cell in 90° to the FAGE cell. Either you show more detailed results to make it clear and visible why the straight version is better than the 90° version (for example by showing zero air decays from both set-ups) or you just mention it in the manuscript, but a Figure is not needed.

We have removed the figure showing the instrument configuration with sampling at 90°.

- If I understand right, the entire system (photolysis cell including the laser and FAGE cell) are located on the roof of the container. Why do you not install it within the container? Is it to save space or to avoid tubing which would be necessary for connecting the photolysis cell if located inside the container? Being on the roof, the temperature in the photolysis cell can vary a lot, I guess you take this into account when calculating the OH reactivity? Please mention somewhere.

The OH reactivity instrument is generally housed on the roof of the container for field experiments and in the laboratory when sampling from HIRAC to minimise the length of the sampling lines. During field experiments, the temperature in the reactivity instrument is the same as the ambient temperature and calculations for OH reactivities are performed at the relevant temperature. Thus far, only room temperature measurements have been made when

sampling from HIRAC, and the temperature in the OH reactivity instrument is again the same as that in HIRAC. We have added the following comment to lines 183-185:

*During laboratory and chamber measurements the instrument is configured within the laboratory. Thus, for ambient measurements, and laboratory and chamber measurements made at room temperature, the temperature in the OH reactivity instrument is the same as the source of the air being sampled.*

**- What is the repetition rate of the photolysis laser used during normal running conditions?**

The repetition rate of the photolysis laser is typically 1 Hz, and has been varied between 0.1 and 1 Hz with no observed effect on the measured OH reactivity, as mentioned in lines 315-316 of the manuscript

**- line 228, it is written that for the 90 ° configuration "the observed OH decays in such a configuration displayed biexponential behaviour, comprising a fast initial decay followed by a slower decay representative of the expected OH reactivity, as observed in previously described instruments (Sadanaga et al., 2004a; Lou et al., 2010)." The reason for the biexponential decay is explained as following (line 237): Once mixing of the air having experienced the photolysis laser with that outside the beam diameter has occurred sufficiently to give uniform OH concentrations in the reaction cell the observed OH decay will result from the chemical losses in the instrument, leading to biexponential decays. Later you mention that in your end on configuration "biexponential decays can still be obtained if the photolysis laser is not correctly aligned along the axis of the reaction cell". Could you give more comments about the respective effect on the decay profile of the beam size (tested?) and alignment for both configurations?**

Limited results were obtained with the instrument configured to sample at 90° once we were able to show that biexponential decays could be avoided by sampling from the end of the reaction cell. A full investigation of the effects of beam size and alignment was therefore not performed with the instrument sampling at 90° and we have included details of the 90° sampling here only to highlight that issues with this instrument design can be avoided by sampling from the end of the reaction cell. When sampling at the end of the reaction cell, poor alignment and/or insufficient beam diameter of the photolysis laser is immediately apparent in the OH decays, and we prefer to focus on results obtained with good alignment which are representative of those obtained in the field and in laboratory experiments.

**- In the section 2.1, you say you draw 12 to 14 slm through the cell of which around 4slm is drawn into the FAGE cell? Can you be more precise on the design of the outlets? Is there just one outlet connected to the fan or several or is the cell designed in a way to pump evenly over the full circumference of the cell in order to maintain the laminar flow and to probe only air from the center of the photolysis cell into the FAGE? I would imagine that with just one outlet for the overflow you would draw gas from the reactor wall opposite of the overflow outlet towards the FAGE inlet orifice, which should have some impact on the k(phys).**

The connection between the reaction cell and the extraction fan originally consisted of a single outlet, as shown in Figure 1. More recently, this has been replaced with an outlet that draws air out of the cell over the full

circumference of the cell. Although the data recorded with the new outlet is not reported in this paper, we do not see any significant change in  $k_{\text{phys}}$  between the different outlet designs, but this will be discussed in future publications. We have added the following comment to the manuscript (lines 191-194):

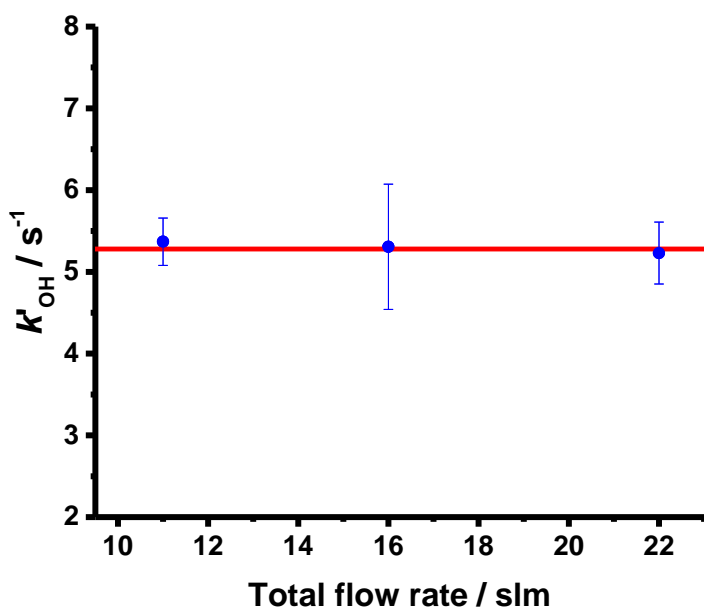
*More recently, the connection between the reaction cell and the exhaust has been replaced with an exhaust that draws air out of the cell over the full circumference of the cell. Although the data recorded with the new exhaust is not reported in this paper, we do not see any significant change in results between the different exhaust designs, but this will be discussed in future publications.*

**- Also, please give the model of the fan and the fan speed used for extraction.**

We have added the model (612F, DC Axial Fan, EBM-Papst) on line 189. The fan speed is set to achieve the desired flow 12-14 slm.

**- Line 475 you say that a total gas flow between 10 and 22 slm did not have any impact on the obtained rate constant of  $n\text{-C}_4\text{H}_9\text{OH}$ . Did you test the instrument without any extra outlet? If yes, what was the difference? I am wondering, if the flow rate has an impact on the intercept, i.e. the  $k(\text{phys})$ ? I could imagine that higher flow rates create higher turbulences and thus higher  $k(\text{phys})$ ? Can you comment on that? Maybe you could show a figure with  $k(\text{phys})$  obtained with 10 and with 22 slm.**

Investigation of effects of total gas flow on the obtained rate constant was performed at a fixed concentration of  $n\text{-C}_4\text{H}_9\text{OH}$  at various total flow rates of gas through the instrument, with no changes made to the outlet. While we did not investigate the effects of the total gas flow on  $k_{\text{phys}}$  directly, the observed rate constant describing the OH decay was unaffected by changes in the total flow rate. Given that the  $n\text{-C}_4\text{H}_9\text{OH}$  was maintained at a constant concentration throughout these experiments, the observation of a constant OH decay profile indicates that  $k_{\text{phys}}$  was unaffected by the change in total flow. We show the reactivity as a function of the total flow below.



**- How exactly do you determine your  $k(\text{obs})$ , does the exponential fit goes always over the same time period? At what delay after the photolysis laser do you start the fit and how did you decide on the starting point? When does it end and how did you decide?**

The time period over which the data are fitted is varied according to the rate of decay of the OH signal (i.e. the OH reactivity), such that data are typically fitted until the OH signal is at the pre-photolysis level to find  $k_{\text{obs}}$ . The fits are started within 5 ms of the maximum in the OH signal, and are ended after the OH signal is essentially back to its baseline value prior to photolysis. Given that the data obtained with this instrument are well represented by first-order decays, the time period over which the decays are fitted does not impact the observed kinetics. We have added the following text to the manuscript (Section 3, lines 364-368) to provide further explanation of the fitting process:

*Fits are typically started within 5 ms of the peak in the OH signal, and data are fitted until the OH signal is essentially back to the background level by the end of the fit. Values for  $S_{\text{OH},0}$  and  $k_{\text{loss}}$  are permitted to vary in the fitting process, since the OH decays are well described by first-order kinetics the fitted values for  $S_{\text{OH},0}$  and  $k_{\text{loss}}$  do not depend in any way on the time period over which the decays are fitted.*

**If the fit lengths changes depending on  $k(\text{obs})$ , then do you deduce the same  $k(\text{phys})$  for all  $k(\text{obs})$  or do you fit  $k(\text{phys})$  over the same time interval? Please give more details on the data evaluation.**

A single value for  $k_{\text{phys}}$  is determined (from several experiments) independently of any measurements of  $k_{\text{obs}}$ , and is fitted over as much of the observed OH decay as possible using the procedure described above in order to obtain the best possible determination of  $k_{\text{phys}}$ . Determinations of  $k_{\text{phys}}$  (and  $k_{\text{obs}}$ ) are independent of the time period over which the data are fitted since the observed OH decays follow first-order kinetics and can be described with a single exponential function. Fitting  $k_{\text{phys}}$  over as much of the decay as possible reduces the uncertainty in the fit. We have added the following text (lines 405-410):

*A single value for  $k_{\text{phys}}$  is determined (from several experiments) independently of any measurements of  $k_{\text{obs}}$ , and is fitted over as much of the observed OH decay as possible using the procedure described above in order to obtain the best possible determination of  $k_{\text{phys}}$  since fitting  $k_{\text{phys}}$  over as much of the decay as possible reduces the uncertainty in the fit. As described above, determinations of  $k_{\text{phys}}$  (and  $k_{\text{obs}}$ ) are independent of the time period over which the data are fitted since the observed OH decays follow first-order kinetics and can be described with a single exponential function.*

**- In Figure 4, the intercept seems to be very close to zero for  $\text{CH}_4$  and  $\text{C}_4\text{H}_9\text{OH}$ : did you deduce  $k(\text{phys})$ ? For OH + CO it is clearly not zero: why?**

Intercepts for all three plots shown in Figure 4 are similar. However, the scale of the y-axis showing the data for OH + CO is such that the intercept appears more significant as it is a higher fraction of the maximum value shown. The intercepts for each plot are  $1.1 \text{ s}^{-1}$  (OH+CO),  $1.3 \text{ s}^{-1}$  (OH+ $\text{CH}_4$ ) and  $1.1 \text{ s}^{-1}$  (OH +  $n\text{-C}_4\text{H}_9$ ). We have added this information to the figure caption.

- Did you estimate the potential bias due to RO<sub>2</sub> radicals within the cell as this could impact the OH decay in two different ways: OH recycling from the reaction of RO<sub>2</sub> in presence of NO can slow down the decays while reaction of OH with RO<sub>2</sub> can accelerate the decays. Indeed, the rate constant for the reaction of peroxy radicals with OH has recently been measured and has been found to be very fast (Bossolasco et al, Chemical Physics Letters, 593, 7-13 (2014), and Farago et al, Chemical Physics Letters, 619, 196 (2015) for CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, respectively), From this work, a tentative rate constant of 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> for the reaction of all peroxy radicals with OH can probably be considered for a rough estimation of the possible impact. Therefore each 10<sup>10</sup> cm<sup>-3</sup> RO<sub>2</sub> would lead to an increase of the OH reactivity of 1 s<sup>-1</sup> while the deceleration due to NO will depend on the NO concentration. The concentration of RO<sub>2</sub> radicals in the volume entering the FAGE system might be quite high for several reasons:

(a) You have a very short inlet line to the reaction cell, so peroxy radicals present in the atmosphere probably reach your cell: from your MCM models you should be able to estimate the RO<sub>2</sub> concentration present outside, which could be taken as an upper limit for the RO<sub>2</sub> concentration entering the FAGE cell. Even under moderate NO<sub>x</sub> concentrations, a large fraction of these RO<sub>2</sub> radicals will probably survive the 7 sec before reaching the FAGE inlet.

This is a valid point, but any peroxy radicals sampled from ambient air would represent a real contribution towards the observed OH reactivity and should (and will) be considered in any calculations or modelling of OH reactivity for comparison with observations.

(b) Peroxy radicals will be produced in the reaction cell due to reactions of VOCs with the photolytically generated OH radicals. You estimate that you produce a concentration of 10<sup>9</sup> cm<sup>-3</sup> OH-radicals per photolysis shot (line 350). These OH radicals will produce a concentration of RO<sub>2</sub> radicals on the same order of magnitude. As the residence time of the gas in the reaction cell is 7 to 8 sec (line 190), the gas is probably photolysed 7 to 8 times before reaching the FAGE intake. Accumulation of reaction products over several laser shots can therefore increase the concentration of RO<sub>2</sub> to near 10<sup>10</sup> cm<sup>-3</sup>.

To investigate this, and other comments below, we have included an additional section (Section 6) in the manuscript describing potential interferences in measurements of ambient OH reactivity by the instrument described in this work. We have performed model simulations of the behaviour in the reactivity instrument to investigate the potential effects of NO, RO<sub>2</sub> and VOC photolysis on the apparent OH reactivity by comparing the true OH reactivity in the model to the OH reactivity determined by analysing the model output simulating the change OH concentration in the reactivity instrument under various scenarios. The results of these model simulations are now described in the manuscript in Section 6 (lines 465-527).

As stated above, a concentration of ~10<sup>10</sup> cm<sup>-3</sup> of RO<sub>2</sub> could potentially contribute ~1 s<sup>-1</sup> to the observed OH reactivity. However, this is less than the overall uncertainty in the OH reactivity measurements, and is an upper estimate as any RO<sub>2</sub> radicals produced within the reactivity instrument will also undergo other chemical and physical losses. In addition, the full effect of the RO<sub>2</sub> radicals will only be evident once all the OH has been titrated to RO<sub>2</sub>. Variation of the repetition rate of the photolysis laser would result in a difference in the concentration of any RO<sub>2</sub> species produced in the cell and thus a difference in the impact of OH + RO<sub>2</sub> on the observed OH reactivity, and

laboratory tests with CH<sub>4</sub> would likely show effects of CH<sub>3</sub>O<sub>2</sub> production if there were an impact of RO<sub>2</sub> radical production. We observed no significant change in the OH reactivity on variation of the repetition rate of the photolysis laser between 0.1 Hz and 1 Hz.

**(c) Peroxy radicals could be produced by the direct photolysis of the ambient VOCs at 266nm. You use 50 mJ / pulse, with a 10mm diameter ≈60 mJ / cm<sup>2</sup>. Taking acetone as an example, ≈0.4% will be photolysed at each laser shot. Accumulation over several laser shots can add up to a total photolysis yield of 2 or 3%, which can lead each to 2 peroxy radicals. With 20 ppb as an example (≈5e11 cm<sup>-3</sup>) this could lead to up to 3e10 cm<sup>-3</sup> of peroxy radicals. Summing up all these possible RO<sub>2</sub> sources, the OH reactivity might be increased by a few s<sup>-1</sup> due to the reaction RO<sub>2</sub> + OH, while it might be at the same time decelerated depending on NO concentration. Of course there is diffusion between two laser shots, decreasing the concentration of laser-made RO<sub>2</sub> radicals, but this process is probably rather slow, given you have laminar flow at ambient pressure. With k(phys) ≈ 1 s<sup>-1</sup> for OH radicals, 36% are still present after 1 s; RO<sub>2</sub> radicals being bigger, they have a smaller diffusion coefficient and the residual concentration after 1 s is probably higher than 36%. Line 312 you say that you have varied the photolysis energy between 1 and 0.1 Hz, which in principle is a good test on the influence of laser made interferences. However, I am doubtful about the feasibility of such experiments in the field: acquiring OH decays good enough to test for such interferences with a repetition rate of 0.1 Hz needs a long averaging time and hence the air mass might have changed in-between a measurement at 0.1 and 1 Hz. I think the coupling to the HIRAC chamber would be a good test as conditions can be kept stable: maybe you have done this already? If yes, could you show some more detailed results? The possible influence of RO<sub>2</sub> radicals on the OH decays has already been mentioned in a recent intercomparison of OH lifetime instruments (Hansen et al. Atmos. Meas. Tech., 8, 4243–4264, 2015), but a much lower pulse energy at a larger beam diameter was used for estimation. Also; no further modelling has been carried out in that work to estimate the converse influence of NO. The current paper might be a good opportunity to go into more detail into this question.**

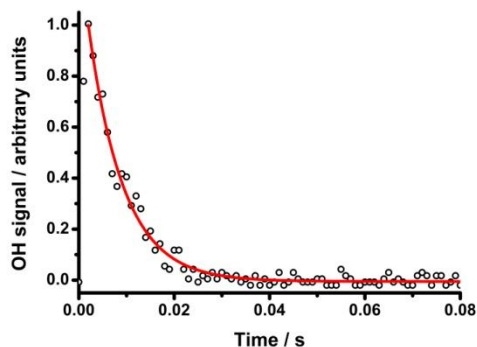
The potential effects of VOC photolysis and RO<sub>2</sub> radical production have been investigated in the model simulations described above, and are now discussed in Section 6 of the manuscript. We find little impact of RO<sub>2</sub> on the retrieved OH reactivity.

Experiments in which the repetition rate of the photolysis laser was varied between 0.1 and 1 Hz were performed for identical averaging periods, both performed in the field, at a time when the observed OH reactivity was relatively constant, and in the laboratory during measurements of rate coefficients for reactions of OH with CO, CH<sub>4</sub> and *n*-C<sub>4</sub>H<sub>9</sub>OH (performed with the instrument coupled to HIRAC). These results are contained within the data shown in Figures 4, 5 and 7 as the results obtained with a repetition rate of 0.1 Hz did not show any significant difference from those obtained at 1 Hz.

**- In section 7 you say, decays of up to 150 s<sup>-1</sup> are scattered (what is the standard deviation?), but can nevertheless be fitted reliably. It would be interesting to see such a decay with the corresponding fit.**

The results of the fits are shown in Figure 4. For OH reactivities of  $\sim 35 \text{ s}^{-1}$ , the standard fit error is  $\sim 0.8 \text{ s}^{-1}$  and the precision is  $\sim 1 \text{ s}^{-1}$ . For reactivities of  $\sim 150 \text{ s}^{-1}$ , the fit errors vary from  $\sim 5 \text{ s}^{-1}$  to  $\sim 16 \text{ s}^{-1}$ , with poorer precision than for lower reactivities. We show an example decay and fit below to demonstrate the reliability of the fit, but believe that this would add little to the manuscript above those already shown.

The red in the example decay gives the fit to the data, giving  $k'_{\text{OH}} = (135.6 \pm 4.5) \text{ s}^{-1}$ .



**- Line 233: you say the air that has not experience the photolysis laser, contains only ambient OH concentration: I doubt that ambient OH radicals survive very long within the reaction cell.**

We agree that ambient OH will not survive very long, and were intending to emphasise that air not having experienced the photolysis laser will have significantly lower (or zero) OH concentrations than air that has experienced the photolysis laser. We have amended the statement (lines 238-242, copied below) to clarify this.

*The air sampled in to the detection cell thus likely contains air that has experienced the photolysis laser (containing elevated OH concentrations) and air that has not experienced the photolysis laser (which will have significantly lower or zero OH concentrations), with this mixing of air potentially leading to an apparent increase in the initial OH decay rate owing to dilution of the air containing elevated OH concentrations with air containing lower (or zero) concentrations.*

**I think the sentence in line 439 is not complete.**

We apologise for the error and have corrected the sentence (now line 550 and referring to Figure 9).

*Figure 9 shows the average diurnal during this period.*

## Review 2

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 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?**

The decays observed with sampling at  $90^\circ$  at long reaction times are consistent with those sampling at the end of the reactor, as mentioned in the manuscript (Section 2.2, lines 230-232). Limited results were obtained with the instrument configured to sample at  $90^\circ$ , and all field and chamber measurements have been taken with sampling at the end of the reactor. We prefer to focus on the instrument configuration and results with sampling at the end of the reactor, and merely aim to point out that biexponential decays can be avoided by sampling 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?**

While we do consider the potential for recycling of OH within the reactivity instrument, under normal operating conditions we do not see any evidence for such effects. High mixing ratios of NO (up to 75 ppb) were observed during the ClearLo campaign, with OH decays measured by the OH reactivity instrument well described by single exponential decays throughout the campaign. We did not observe any biexponential decays for any conditions



encountered during the campaign, indicating that recycling of OH in the reactivity instrument through reactions of NO was minimal.

We have included an additional section (Section 6) in the manuscript describing potential interferences in measured OH reactivity which includes effects of NO on recycling of OH within the reactivity instrument. Model simulations indicate that potential interferences caused by recycling of OH are minimal for the instrument described in this work.

**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?**

Please see responses above to comments from reviewer 1 where details of the fitting procedure are given. Time zero is always defined at the time point at which the photolysis laser is fired, and, given the rate of OH production following firing of the photolysis laser, the OH production can be considered as being instantaneous. Since the OH decays are first-order and well-described by a single exponential function the time period over which decays are fitted does not influence the fit results. We have included additional information in Section 3, lines 364-368 (copied above in response to reviewer 1).

**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.**

The paper addressing this issue has now been accepted for publication (Stone et al., 2016), and describes the phenomenon in detail. It is not a result of any interference leading to formation of OH inside the FAGE cell, nor recycling through any peroxy radical reactions, but a physical effect resulting from convolution of the kinetics of the OH decay with the effects of velocity distribution on the time taken for sampled gas to travel from the point of sampling to the point of detection. OH reactivities of up to at least  $150 \text{ s}^{-1}$  can be measured reliably with this instrument, as stated in the manuscript (line 500). There is no dependence on NO concentration as the effect is not chemical. We have included some additional details in the discussion in Section 9 (copied below), but note that a full discussion is beyond the scope of this work and is discussed in detail in Stone et al. (2016).

*However, recent work in Leeds has shown that, at higher reactivities, observed kinetics can be influenced by sampling issues related to the effects of velocity distributions on the transport time of sampled gas from the pinhole nozzle to the point at which fluorescence is excited and detected in the FAGE cell. The effects of the velocity distributions on*

*the time taken for sampled gas to travel from the pinhole to the point of detection coupled with the true kinetics of the OH decay can lead to underestimations of very high reactivities, and is described in detail by Stone et al. (2016).*

**5) There is also little discussion of potential interferences, such as the production of HO<sub>2</sub> 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?**

Please see above responses to comments from Reviewer 1. We have added a section (Section 6) discussing potential interferences and describing a number of model simulations under various scenarios to investigate the possible effects of OH recycling through reactions of HO<sub>2</sub> and RO<sub>2</sub> radicals with NO, and of production of HO<sub>2</sub> through photolysis of oVOCs such as HCHO. There is no significant impact of these effects on the measured  $k'_{OH}$ .

### Review 3

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 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).**

We have included these data in the abstract (copied below).

*The instrumental limit of detection for  $k'_{OH}$  was determined to be  $1.0\text{ s}^{-1}$  for the campaign in London and  $0.4\text{ s}^{-1}$  for the campaign in York. The precision, determined by laboratory experiment, is typically  $< 1\text{ s}^{-1}$  for most ambient measurements of OH reactivity. Total uncertainty in ambient measurements of OH reactivity is  $\sim 6\%$ .*

**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.**

We have added the following comment to the manuscript (line 40-42):

*Similarly, when model calculations show poor agreement with observations, it can be problematic to determine whether the model discrepancies result from incomplete knowledge of the total production rate or of the total loss 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.**

We have changed the phrase to refer to the contact time.

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

We have added the references for PTRMS (Sinha et al., 2008) and GC-PID (Nolscher et al., 2012) instruments. We apologise that the GC-MS should have been listed as a separate PTRMS instrument using ToFMS (Michoud et al., 2015) as opposed to QMS and have corrected this.

**P3 L95: It is mentioned that the correction to apply on the CRM measurements requires knowledge of HO<sub>2</sub> and NO. It is wrong. Only NO is needed.**

We apologise for the error and have corrected the statement as shown below:

*"...knowledge of NO concentrations are required to correct for any interferences..."*

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

We have clarified the statement to indicate that OH is produced without simultaneous production of HO<sub>2</sub>:

*The laser flash photolysis technique produces OH in isolation (i.e. with no simultaneous production of HO<sub>2</sub>)...*

**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.**

We have removed the equation.

**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?**

We have clarified the description in Section 2.4 (lines 318-320 in the revised manuscript, copied below). The pulse is typically 1 Hz. Although the gas reaction cell is not completely refreshed between laser pulses, experiments in which the pulse repetition frequency of the photolysis laser was varied between 0.1 and 1 Hz indicate that there is little impact on the observed OH reactivity (please see also responses to comments by Reviewer 1).

*The data collection cycle, as illustrated in Figure 2 is typically repeated every 1 s (i.e. with the photolysis laser having a pulse repetition frequency of 1 Hz). Experiments, both in the laboratory and in the field, in which the PRF of the photolysis laser was varied between 0.1 and 1 Hz showed no effect on the observed OH reactivity.*

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

While the cell is calibrated we do not typically determine the absolute concentrations of OH in the reaction cell. The OH signal produced on photolysis must be high enough to enable the observation of the subsequent OH decay. For low ambient O<sub>3</sub>, the OH signal obtained on photolysis is low and is increased by the addition of a small flow of humidified air containing O<sub>3</sub>.

**P5 L213-215: Since a mercury lamp is used to produce O<sub>3</sub> in a small flow of humid air OH and HO<sub>2</sub> radicals will also be produced from water photolysis at 185 nm. Could a significant amount of H<sub>2</sub>O<sub>2</sub> be produced from OH+OH and HO<sub>2</sub>+HO<sub>2</sub> reactions before the air flow reaches the sampling reactor? And as a consequence could a significant OH reactivity be generated from OH+H<sub>2</sub>O<sub>2</sub>?**

While there will be some photolysis of H<sub>2</sub>O, the concentrations of OH and HO<sub>2</sub> produced are likely to be low, with little formation of H<sub>2</sub>O<sub>2</sub>. The flow of humid air containing ~50 ppb of O<sub>3</sub>, generated by the mercury lamp, is used during experiments to determine  $k_{\text{phys}}$  and thus any impact of H<sub>2</sub>O<sub>2</sub> production on the observed reactivity would be

evident in measurements of  $k_{\text{phys}}$ . Given that  $k_{\text{phys}}$  has been determined to be  $1.1 \text{ s}^{-1}$  during ClearfLo and  $1.25 \text{ s}^{-1}$  during the York campaign, this places an upper limit of  $1.25 \text{ s}^{-1}$  on the effect of  $\text{OH} + \text{H}_2\text{O}_2$ , assuming that other losses of OH are zero. Given that 50 ppb of  $\text{O}_3$  is formed by the lamp, at 1 % humidity approximately  $1 \times 10^{11} \text{ cm}^{-3}$  of OH and  $\text{HO}_2$  could be produced in the lamp region, leading to a maximum of  $\sim 2$  ppb  $\text{H}_2\text{O}_2$  from  $\text{HO}_2 + \text{HO}_2$  and  $\text{OH} + \text{OH}$  which would result in a reactivity of  $< 0.1 \text{ s}^{-1}$ . In any case, it is likely that any OH or  $\text{HO}_2$  produced by photolysis of water vapour will be lost to the walls of the tubing connecting the gas flow to the reactivity instrument. Moreover, any impact of  $\text{H}_2\text{O}_2$  production would display a trend with the lamp current applied to the mercury lamp, which was not observed during measurements of  $k_{\text{phys}}$ .

**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?**

We agree it is unlikely that ambient OH survives through the sampling line, and have rephrased this statement (lines 238-242 in the revised manuscript, see also the responses to reviewer 1).

**P8 L349-P10 L353: Please indicate the range of water concentrations used for calibration.**

The water vapour concentration is typically varied between 300 and 10,000 ppm during calibration experiments. We have added this information to the manuscript (lines 357-358).

**It is mentioned that  $1\text{E}9 \text{ cm}^{-3}$  of OH is produced in ambient air by the pump laser. Please also report the  $\text{O}_3$  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  $1\text{E}7 \text{ cm}^{-3}$ . The signal-to-noise ratio used to calculate the detection limit and the integration time should also be reported.**

The signal-to-noise ratio ( $1\sigma$ ) and integration time (5 min) have been added to the manuscript (lines 357-359).

The concentrations of  $\text{O}_3$  and  $\text{H}_2\text{O}$ , and thus initial OH concentration, are highly variable during field experiments. As discussed above, knowledge of the absolute OH concentration is not necessary to determine the OH reactivity. At 266 nm, the absorption cross-section of  $\text{O}_3$  is  $9.65 \times 10^{-18} \text{ cm}^2$  (Atkinson et al., 2004), for a minimum ambient  $\text{O}_3$  concentration of 10 ppb (below which  $\sim 50$  ppb is added to the instrument), typical laser fluence of  $\sim 50 \text{ mJ cm}^{-2}$  (given in Section 2.1) and a quantum yield for production of  $\text{O}(^1\text{D})$  of 0.9 (Matsumi et al., 2002), the initial  $\text{O}(^1\text{D})$  concentration is  $\sim 1.6 \times 10^{11} \text{ cm}^{-3}$ . For a water vapour concentration of  $5 \times 10^{17} \text{ cm}^{-3}$  ( $\sim 2\%$ ), competition between reaction of  $\text{O}(^1\text{D})$  with water, leading to 2 OH, and quenching of  $\text{O}(^1\text{D})$  by  $\text{N}_2$  or  $\text{O}_2$ , to produce  $\text{O}(^3\text{P})$ , typically produces  $\sim 3 \times 10^{10} \text{ cm}^{-3}$ . The  $10^9 \text{ cm}^{-3}$  reported in the paper is thus an underestimate and we have corrected this in the manuscript and show the calculation (lines 362-369), copied below.

*For a minimum ambient  $\text{O}_3$  mixing ratio of 10 ppb (below which  $\sim 50$  ppb is added to the instrument (Section 2.1), an absorption cross-section for  $\text{O}_3$  of  $9.65 \times 10^{-18} \text{ cm}^2$  at 266 nm (Atkinson et al., 2004), typical laser fluence of  $\sim 50 \text{ mJ cm}^{-2}$  and a quantum yield of 0.9 for production of  $\text{O}(^1\text{D})$  (Matsumi et al., 2002), the initial  $\text{O}(^1\text{D})$  number density following photolysis is  $\sim 1.6 \times 10^{11} \text{ cm}^{-3}$ . For a water vapour concentration of  $5 \times 10^{17} \text{ cm}^{-3}$  ( $\sim 2\%$ ), competition between reaction of  $\text{O}(^1\text{D})$  with water ( $k_{\text{O}^1\text{D}+\text{H}_2\text{O}} = 2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (Atkinson et al., 2004)), leading to 2 OH, and*

quenching of  $O(^1D)$  by  $N_2$  ( $k_{O1D+N2} = 3.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Atkinson et al., 2004)) or  $O_2$  ( $k_{O1D+O2} = 4.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Atkinson et al., 2004)), to produce  $O(^3P)$ , typically leads to an initial OH concentration in the reactivity instrument of  $>3 \times 10^{10} \text{ cm}^{-3}$ , in agreement with the calibration results.

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

During the ClearLo campaign, the uncertainty in the measured OH reactivity is  $\sim 6\%$ . The uncertainty in  $k_{\text{phys}}$  contributes, on average, 70% to this uncertainty. Uncertainties related to dilution represent  $\sim 25\%$  of the total uncertainty when dilution is necessary. We have added this information to the manuscript (lines 460-463, copied below).

*On average, the total uncertainty in measurements of  $k'_{\text{OH}}$  is 6%, with the uncertainty in  $k_{\text{phys}}$  comprising  $\sim 70\%$  of the total uncertainty. When addition of  $O_3$  to the instrument is necessary to improve the OH signal (at ambient mixing ratios of  $O_3$  of less than 10 ppb and during laboratory experiments and measurements of  $k_{\text{phys}}$ ), the uncertainty associated with the dilution of the main flow contributes  $\sim 25\%$  to the total uncertainty in  $k'_{\text{OH}}$ .*

**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?**

The main species present was CO, at mixing ratios of up to 170 ppb (despite the use of scrubbing agents designed to remove to sub-ppb levels), leading to a reactivity of  $<1 \text{ s}^{-1}$ . The intercepts of calibration plots using calibration standards, run at varying flow rates and concentrations, indicated that the peaks did not arise from internal contamination of the GC instrument.

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

The standard deviation given reflects the variability of  $k_{\text{phys}}$  over time during each campaign. The precision of  $k_{\text{phys}}$ , during the ClearLo campaign, determined by repeated measurements, is  $0.4 \text{ s}^{-1}$ . We have added this information to the manuscript (Section 3.1, lines 424-426, and Section 5).

*Determination of  $k_{\text{phys}}$  in the laboratory and in the field for the ClearLo campaign in London in 2012 gave an average value  $(1.1 \pm 1.0) \text{ s}^{-1}$  (precision of  $0.4 \text{ s}^{-1}$ ) and  $(1.25 \pm 0.42) \text{ s}^{-1}$  (precision of  $0.2 \text{ s}^{-1}$ ) for the campaign in York in 2014 (Section 7).*

**P10 L413: Please report the ranges of CO and CH<sub>4</sub> concentrations as well as the 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?**

These data are shown in Figure 4. Replicates were performed, for OH reactivities of  $\sim 35 \text{ s}^{-1}$ , the standard fit error is  $\sim 0.8 \text{ s}^{-1}$  and the precision is  $\sim 1 \text{ s}^{-1}$ . For reactivities of  $\sim 110 \text{ s}^{-1}$  the precision is  $\sim 5 \text{ s}^{-1}$ , and reactivities of  $\sim 140 \text{ s}^{-1}$  have been measured in the field with fit errors of  $\sim 6 \text{ s}^{-1}$ . We have added the following information to the manuscript (Section 5, lines 457-459):

*Replicates of  $k'_{\text{OH}}$  measurements at fixed concentrations of CO and CH<sub>4</sub> (Section 4 and Figure 4) also enable determination of the instrument precision. For OH reactivities of  $< 35 \text{ s}^{-1}$  the precision is  $\sim 1 \text{ s}^{-1}$ , and  $\sim 5 \text{ s}^{-1}$  at reactivities of  $\sim 110 \text{ s}^{-1}$ . In the field, reactivities of up to  $\sim 140 \text{ s}^{-1}$  have been measured, with fit errors of  $\sim 5 \text{ s}^{-1}$ , although the precision at higher reactivities is worse compared to lower reactivities.*

**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)?**

We have included some additional discussion of the modelling study and we have added a new section (Section 5) to discuss the limit of detection, precision and total uncertainty. For the ClearfLo campaign, the  $1 \sigma$  limit of detection was  $1.0 \text{ s}^{-1}$ , while for the York campaign the  $1 \sigma$  limit of detection was  $0.4 \text{ s}^{-1}$ . The precision varies from  $0.4 \text{ s}^{-1}$  for measurements of  $k_{\text{phys}}$  ( $1.1 \text{ s}^{-1}$ ) to  $\sim 5 \text{ s}^{-1}$  for reactivities of  $\sim 110 \text{ s}^{-1}$ , and is  $\sim 1 \text{ s}^{-1}$  for reactivities of  $\sim 35 \text{ s}^{-1}$ . Total uncertainty in  $k'_{\text{OH}}$  is approximately 6 %. We have included an additional section (Section 5 in the revised manuscript) including these data. We have also added the following to the description of the modelling by Whalley et al. (lines 541-546):

*Detailed analysis of these data, including model calculations using the Master Chemical Mechanism constrained to observed concentrations of long-lived species, is described by Whalley et al. (2015). The modelling study shows that the observed OH reactivity can be reproduced by the model (to within 6 %) when larger VOCs than those typically measured are included in the model, and demonstrates the importance of oxidation intermediates and the role of heavy VOCs, particularly biogenics, in controlling the total OH reactivity and the oxidation budget in a megacity such as London.*

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

The higher dilution factor for chamber experiments compared to ambient measurements (where there is little or no dilution), leads to higher absolute uncertainty in chamber measurements of OH reactivity. However, since the uncertainty is related to the uncertainty in the calibrations of the mass flow controllers, which are similar for the

different dilutions, the relative error in the observed reactivity is similar for experiments requiring large dilution to those with smaller dilution. Errors in the mass flow controller calibrations are approximately 5 %, and the uncertainty in the dilution contributes ~25 % to the total uncertainty in  $k'_{\text{OH}}$ . We have added the following statement to the manuscript (lines 576-577):

*The uncertainty associated with the dilution contributes ~25 % to the total uncertainty in  $k'_{\text{OH}}$ , which is approximately 6-8 %.*

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

We have added some additional information regarding this issue (please also see responses above where the additional text is shown), with a full discussion given in a separate publication (Stone et al., 2016). Bimolecular reactions of OH inside the FAGE detection cell are minimised by the reduction in pressure on entering the FAGE cell, and do not affect the observed OH time profile.

**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.**

The chronogram is discussed in the caption (“Four 50  $\mu\text{s}$  wide photon counting bins cover the time period between each 308 nm laser pulse, but only the bins immediately after the laser pulse collect any fluorescence photons (shaded bins), and only the photon counts from these bins are used to construct the OH decay.”). We believe the chronogram aids understanding of the photon counting method used in this work.

**Figure 3: Why does OH increase over 15 ms after the laser pulse? Is it due to the  $\text{O}(^1\text{D})+\text{H}_2\text{O}$  kinetic? How long after the laser pulse did you choose to start the fit? Why?**

The production of OH from  $\text{O}(^1\text{D})+\text{H}_2\text{O}$  is rapid (effectively instantaneous on the timescale of this instrument), and is not the cause of the observed increase in OH signal. The production of OH from  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ , and the relaxation of any vibrationally excited OH formed in the reaction, is expected to be complete within 1  $\mu\text{s}$ . The observed increase results from the transport time of OH radicals from the point of sampling into the FAGE cell (i.e. from the pinhole) to the point at which 308 nm excitation and detection occurs. This feature is common for all pump-probe OH reactivity instruments, and has little impact on the observed OH reactivity at typical ambient reactivities (further discussion on the effects on measurements of fast kinetics is discussed in detail by Stone et al., 2016). The fit to the data is started just after the maximum OH signal, and, as discussed above, the time point after the peak where the fit begins does not affect the fit results for a first-order decay.

**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?**

The error bars shown are the fit errors. We have clarified this in the caption.



## References

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