

We would like to thank both referees for their useful comments. We have responded to all the comments below in bold:

Anonymous Referee #1

Received and published: 16 August 2013

The authors report the investigation of the measurement sensitivity of an instrument for the detection of atmospheric HO₂ applying laser-induced fluorescence (LIF). This is an important work because of recently discovered interferences from RO₂ radicals. Since the magnitude of this interference is specific for every instrument, this work gives new information about the HO₂ measurements done by this group in the past and consequences for measurements in the future. Furthermore, the authors develop an approach utilizing this interference, in order to estimate the concentration of certain RO₂ types. Therefore, the topic of this work fits well within the scope of AMT. The authors carefully characterized their instruments and present the results in a well-written paper. Publication in AMT is recommended after addressing the following points:

Time resolved measurements: The authors report time resolved measurements, in order to determine OH yields from interfering RO₂ by using an instrument which combines laser flash-photolysis and LIF. It is not fully clear from the manuscript, what the advantages of this method are compared to the determination of the magnitude of the interference using the steady state approach (also reported in the paper). Both methods finally give the OH yield from RO₂ radicals. The quality of both methods seems to be comparable (Table 1 and 2). However, a different measurement cell than used in field applications is taken for the time resolved measurements. Although this measurement cell is similar to the one used in the field, only the characterization of the field instrument reported in the paper gives important information about HO₂ from field campaigns in the past. The measurements with the time resolved instrument confirm the results obtained by the steady state approach, but does not add new results. Please address the following points in more detail: (1) What is the additional value of these measurements?

By running the time-resolved experiments, we gain information on the kinetics of the processes taking place. Figure 3, lower panel, demonstrates that the titration of RO₂ radicals to OH in the presence of NO is rapid, consistent with fast decomposition of β -hydroxyalkoxy radicals and consistent with known MCM chemistry. Other potential sources of HO₂ that have been suggested in the literature such as HO₂ production from the 1,6 shift of δ -hydroxy-peroxy radicals formed from isoprene (Peeters et al. 2009) would form on the second time-scale and so by looking at the time-resolved experiment we can be confident in the process that we are studying.

(2) Why is the pressure in the flow tube reduced to 300 torr (p6260 l20)? What are the consequences for the conclusions of these experiments?

The OH signal observed was greatest at 300 Torr and decreased significantly at higher pressures. This feature of the experiment may reflect a FAGE sampling issue, with the properties of the jet changing as the flow tube pressure changes. For reactions initiated by OH abstraction, no pressure dependence is expected. For reactions which proceed via OH addition, a pressure dependence is expected, but at 300 Torr and beyond this reaction will have reached the high pressure limit. Similarly, further reactions of the alkyl radical, i.e. $R + O_2 + M \rightarrow RO_2 + M$ will be pressure dependent, but, again, is at the high pressure limit above 300 Torr and so we do not expect the conclusions drawn from these experiments to change with pressure changes between 300 – 760 Torr.

(3) Why is the oxygen content of the air less than 10% (p6261 l22-24)? What are the consequences for the conclusions of these experiments?

We ran the experiments in N₂ and added sufficient O₂ to the system for RO₂ radical formation, and titration of RO₂ radicals to OH (R6 – R11). In these reactions, reaction with O₂ is not the rate determining step and so we expect the conclusions drawn from the experiments presented to be the same as experiments run with 20% O₂. Running a model simulation with [O₂] doubled under the time-resolved experimental conditions yields the same [OH] as in model simulations with [O₂] reduced by 50%. We will include a discussion of this in the revised manuscript.

(4) Please give a lifetime for the reaction of OH with the VOC in the flow-tube on p6262 and compare this with the residence time in the flow-tube.

Considering isoprene, at a typical concentration of 1×10^{13} molecule cm⁻³ (as used in the experiments) we can estimate a pseudo-first-order rate of removal of OH of > 1000 s⁻¹, and so the lifetime of OH is $< 10^{-3}$ s; this compares to the residence time in the flow tube before sampling by FAGE of ~ 4 s.

(5) Please give numbers for the loss rate of OH and HO₂ in the flow tube in the absence of reactants. How does this time constant compare to the lifetime of OH in the presence of the VOC?

The OH reactivity, in the absence of a VOC, was dependent on the [O₃] present in the flow-tube which was estimated to vary between $0.88 - 2.65 \times 10^{14}$ molecule cm⁻³ depending on the efficiency of the ozone generator used to fill the ozone bulb, leading to an OH reactivity between $6 - 19$ s⁻¹, and a corresponding lifetime of $0.05 - 0.17$ s. As well as reaction with O₃, non-reactive losses of OH, such as diffusion out of the photolysis beam area can also contribute to the observed loss. The upper panel in figure 3 has been incorrectly labelled as the OH decay in the presence of isoprene, when in fact, this decay was taken in the absence of reagents; the reactivity determined from this exponential decay is ~ 25 s⁻¹ (lifetime of OH 0.04 s)

For HO₂, generated by reaction of OH with methanol in the flow-tube, the reactivity, determined from the exponential decay, is ~ 5 s⁻¹ (lifetime 0.2 s) with diffusion out of the photolysis beam area and radical-radical losses contributing to this observed loss; radical-radical losses are estimated to contribute ~ 1 s⁻¹ to reactivity at the radical concentrations used in these experiments.

(6) In Fig. 3 an OH decay curve in the presence of isoprene is presented, which indicates that OH is converted to RO₂ on a similar time scale as the HO₂ and RO₂ lifetime in the flow-tube (lower panel of Fig. 3). Was the same isoprene concentration used in both experiments shown in the upper and lower figure?

If this was the case, I would expect to see a superposition of the OH decay curve and an increasing signal from the interference, so that a single exponential function (p6265 l24) would not apply. Please comment and discuss the OH decay curve in the manuscript.

The upper panel in figure 3 has been incorrectly labelled as the OH decay in the presence of isoprene, when in fact, this decay was taken in the absence of reagents; the reactivity determined from the exponential decay is ~ 25 s⁻¹. We apologise for the obvious confusion this error has caused.

(7) p6266 l9-21: The authors discuss reasons, why part of the experiment may be influenced by some specific technical problems of their experiment procedure. The authors may want to decide, which measurements were reliable. I would suggest to present only results from these measurements.

Unfortunately, the problems we encountered when introducing methanol into the reaction flow-tube influenced the majority of the yields determined from the comparison with HO₂ yields from methanol, but, we agree, that we should limit the yields given in Table 2 to those we have confidence in and will do so in the revised manuscript.

Reaction time and NO concentration in the measurement cell: The authors give reaction times in the measurement cells, which are derived from interference measurements with different NO concentrations. They assume that the NO concentration in the measurement cell is less than expected. Although it is briefly discussed that the adjustment of the reaction time and of the NO concentration is to some extent equivalent, they decide to adjust the reaction time, because they determined the residence time in earlier experiments for one of the detection cells. Is there a clear indication that these measurements can be transferred to the experiments and measurement cells in this work?

Although we estimate the residence time from the interference measurements and the injected NO (for cell A) and find that the residence time compares favourably with the CFD calculations performed for this cell, we do not think that this means that if experimental conditions, such as the [NO] used and residence time is known for a particular FAGE system, that the level of interference suffered can be determined absolutely. We have found it useful to calculate the residence time in each cell type, assuming plug flow conditions for comparison with estimated residence times determined by agreement with modelled interference yields to highlight this point more clearly:

	Cell A	Cell B	Cell C	Cell D
Plug flow residence time (ms)	40	4	70	4
Estimated residence time by comparison with model (ms)	0.9	1.9	60	9.8

For cell A, the residence time determined assuming plug flow conditions is approximately 44 times longer than residence times determined from CFD calculations and comparison with time-resolved modelled interference yields suggesting that, in reality, the air stream is significantly accelerated within this cell (and in turn will be significantly cooled), owing to the supersonic expansion after the small diameter pinhole. For cell B, the plug flow residence time is ~ 2 times longer, suggesting modest acceleration and modest cooling. Whilst for cell C, the plug flow residence time compares reasonably well (1.2 times slower) with the residence time estimated from model comparisons. In cell C, air enters the FAGE cell through a 4 mm pinhole and so we may not expect the same level of acceleration or cooling as we predict in cell A - we may also expect that NO should mix reasonably well with the air stream in cell C. In the original manuscript we assumed an average internal cell temperature for all cells of 255 K and highlighted the impact of this reduced temperature on the interference yields. For modelled yields and observed yields to agree for cell C, when 255 K was assumed, we made the assumption that NO was poorly mixed into the air stream. By taking into account the factors outlined above, it is more likely that the internal cell temperature of C was closer to ambient. At 298 K, a reasonable model measurement agreement is achieved for cell C for all RO₂ species considered assuming a residence time of 70 ms and [NO] 9.5 x 10¹⁴ molecule cm⁻³. We will update the discussion in section 4 of the revised manuscript accordingly. Interestingly, if we calculate the residence time in the FAGE cell used during the time-resolved experiments (we will call this 'Cell D' for the purpose of this discussion) assuming plug flow conditions we find that the time calculated is shorter, by just over a factor of two, than the residence time assumed by comparison with model yields. We actually obtain reasonable agreement between the two methods to estimate residence time if we assume that the air stream was in contact with NO from pinhole to detection region rather than just in contact with NO from NO injection region to detection region suggesting that in this cell there may have been some back flushing of NO

throughout. Such back flushing served to maximise the level of interference suffered in this cell (and we actually found that it was very difficult to minimise the interference in this cell by reducing the flow of NO injected, in contrast to cell A – Figure 6). For HO₂ detection, free from interferences, we may consider Cell D to be an extremely poor choice, whilst cells, such as cell A, which minimise residence time, minimise [NO] mixed into the ambient air stream and operate at reduced temperatures are optimal. As factors, such as internal cell temperature and the time and distance over which air expands (which will affect the extent to which NO mixes into the ambient air stream) all impact the level of interference suffered for a particular experiment and are very difficult to quantify, every FAGE system used for ambient measurements of HO₂ needs to be characterised explicitly. By considering the level of interference for 4 different cells, we have hopefully highlighted the factors that should be considered when attempting to minimise (or maximise) this interference.

Separation of total RO₂ and “interfering” RO₂: The authors show an approach to separate between HO₂, total RO₂, and specific RO₂, which causes interferences in the HO₂. This is an interesting approach. However, there is one simplification, which complicates the calculation shown here (Eq. 7,8). As indicated in Eq. 7,8 there are different RO₂ species. In Eq. 7,8 it is assumed that the conversion efficiency in the HO₂ is the same for a group of certain RO₂ radicals at higher NO concentrations. As shown in Table 1,2 this is not necessarily true, so that Eq. 7,8 contains more unknown values and requires the knowledge of the RO₂ distribution, in order to calculate HO₂ and RO₂ concentrations. For specific conditions with only few RO₂ species this approach may be applicable (e.g. laboratory experiments as mentioned by the authors), but it may get more complicated for field measurements. In my opinion, this approach becomes more valuable for model-measurement comparisons, when HO₂* is taken from model calculations for the two different measurement modes (NO concentrations) of the HOX detection cell. I would recommend to discuss the limitations of this approach in Section 4.2 in more detail.

For equations 7 and 8 to be totally correct, α must represent the mean conversion efficiency for all RO_{2i} species present, which, in the absence of speciated RO₂ measurements, means that the modelled concentration of each individual RO₂ needs to be determined to calculate the appropriate α to use. By assuming that alkene and aromatic derived RO₂ species represent all RO_{2i} will positively bias [RO_{2i}] and negatively bias [HO₂]. Preliminary box modelling studies run for the ClearLo project, which is constrained by the measurements of a wide range of VOCs of various classes, demonstrate, however, that aromatic and alkene RO₂ species do dominate RO_{2i}, with >C₄ alkane-derived RO₂ species only contributing 7 % to all RO_{2i} identified on average. For this particular environment at least (and likely applicable to many others), we would argue that determining HO₂ and RO_{2i} by the methodology discussed may provide reasonable results. We will however discuss the limitations of the approach further in Section 4.2.

Figure 6: The ratio of the HO₂ to RO₂ is shown depending on the NO concentration. Why are only 4 calculated values are shown? Why are they calculated for different NO concentrations than used in the experiments? What is the meaning of the fit function (the fit function is not used in manuscript)?. In this figure, I would expect to see a model measurement comparison, for which the density of calculated points is large enough to connect them to a line, making a fit function unnecessary.

As suggested, we have now modelled the HO₂:RO₂ signal ratio at many more [NO] and will display this as a line for comparison with the measured ratios determined.

Technical points:

p6258 l5: There is one right parenthesis more than needed after "Leybold"
This will be removed

p6265 l24: Please explain x and y in the general fit function $y=y_0 + A\exp(-Bx)$, so that the reader can easily connect the function to the curves shown in Fig. 3.

We will replace the fit function with: OH signal= $y_0 + A\exp(-B \times \text{probe delay time})$ for clarity.

p6267 L2: The title "Time-resolved model-measurement comparison" does not describe the experiments accurately, because the comparison does not concern the time dependence of the measurement.

We suggest the revised title: "Time-resolved experiments. Measured and modelled HO₂ yields following complete conversion of RO₂".

p6269 l10: I assume that the number of the subsection is missing.

The section numbering will be added

p6271 Section 4.2: Please specify which detection cell was used in the experiments shown here.

It was cell A. This will be stated in the text of the revised manuscript

Table 1,2 and Figure 4,5: What is the additional value of Figure 4 and 5? They show the same as Table 1,2 with only the exception that Fig. 5 contains also modelled values. They could be included in Table 1 in the same way as done in Table 2.

We will add the modelled values to the tables and remove figures 4 and 5 from the revised manuscript.

Figure 4: The caption "Time-resolved OH yields..." does not accurately describe what is shown. OH yields are not time

We will be removing Figure 4, as suggested above, from the manuscript

all Figures: I would suggest to check the readability of all figures regarding the size of dependent. labels and thickness of lines.

Figure readability will be improved in the revised manuscript.

Anonymous Referee #2

Received and published: 5 September 2013

This paper presents measurements of interferences in the detection of HO₂ radicals by various RO₂ radicals in several FAGE instruments used by this group in the past. Recent measurements have shown that detection of HO₂ radicals by chemical conversion to OH through reaction with NO can be sensitive to the detection of select RO₂ radicals. The degree of interference likely depends on the characteristics of the instrument (flow velocity, inlet geometry), thus each individual instrument must be calibrated for this interference in order to accurately interpret past and future measurements using this technique. Similar to other FAGE instruments, these authors find that several of their instrument configurations are sensitive to the detection of alkene and aromatic derived peroxy radicals, and provide some discussion on the impact of this interference on their previous measurements. The paper is well written and appropriate for publication in AMT after the authors have addressed the following comments:

1) The authors present two methods for determining the conversion efficiency of RO₂ into OH – their OH and HO₂ calibration system using a turbulent flow reactor that generates a steady state concentration of radicals using a mercury pen-ray lamp, and a flow tube system that incorporates a time-dependent source of radicals through laser flash photolysis techniques. Unfortunately it is not clear why two of the two different techniques were used, as it appears that each technique was used to calibrate different FAGE instruments. The authors should clarify why the time-dependent source of radicals was used, why the interference for the different field FAGE instruments were not cross calibrated with this technique, and why a fourth FAGE instrument with a different geometry compared to the field instruments was used, which was also not cross calibrated with the steady-state field reactor.

The time-resolved flow tube experiments were not performed on a field instrument used for ambient HO₂ detection and so the purpose of these experiments, rather than gauge the level of interference suffered, was to experimentally determine the yield of OH from a range of RO₂ radicals in the presence of NO to compare to MCM recommendations. The time-resolved experiments enabled long reaction times to be reached, allowing the conversion of RO₂ to OH to proceed to completion, and providing a measure of the asymptotic yields of HO₂.

By running the time-resolved experiments, we gain information on the kinetics of the processes taking place. Figure 3, lower panel, demonstrates that the titration of RO₂ radicals to OH in the presence of NO is rapid, consistent with fast decomposition of β -hydroxyalkoxy radical and consistent with known MCM chemistry. Other potential sources of HO₂ that have been suggested in the literature such as HO₂ production from the 1,6 shift of δ -hydroxy-peroxy radicals formed from isoprene (Peeters et al., 2009) would form on the millisecond time-scale and so by looking at the time-resolved experiment we can be confident in the process that we are studying.

As both methods are in agreement with model predicted yields and consistent with each other, we do not feel it necessary to cross-calibrate the two approaches.

2) For the time-dependent radical source experiments, the authors compare the decay of converted OH radicals in the FAGE instrument from different RO₂ radicals generated in the flow tube, using the coefficient of the exponential as a measure of the converted RO₂ radicals, comparing it to the exponential from the experiments with methanol, which produce only HO₂. The cause of the decay of radicals in the flow tube is not discussed, but self-reactions of the peroxy radicals likely contribute. It is not clear from the discussion why the authors used this approach, and the data shown in Figure 3 is

somewhat confusing. It appears to show that the conversion efficiency of RO₂ to OH is high for isoprene and low for the alkanes. However, without information regarding the relative radical concentrations used in these experiments it is difficult to interpret the different figures. Were the initial OH concentrations (signals) and decay rates in the absence of NO the similar for all experiments, suggesting that the RO₂ concentrations were similar?

There was some variability in signal over the course of all experiments, caused by the variability of [O₃] introduced. Relative yields were determined by running an experiment with a particular RO₂ radical generated back to back with an experiment where either HO₂ was generated (from methanol) or ethene-derived RO₂ radicals were generated. [RO₂] will have remained constant during these back to back experiments enabling a relative yield to be calculated.

Are the decay rates of each consistent with the estimated RO₂ concentration and MCM rate constants?

The decay observed in the lower panel of figure 3 can be attributed primarily to diffusion of radicals out of the photolysis laser beam area and, to a lesser extent, radical-radical reactions: At a RO₂ radical concentration of 5×10^{10} molecule cm⁻³ radical-radical reactions can be estimated to contribute $\sim 1 \text{ s}^{-1}$ to the loss rate observed. It is difficult to compare the decay observed to MCM predictions owing to the contribution of diffusion of radicals out of the photolysis beam area to the observed decay.

It appears that the OH decay in the top panel of the Figure is for a lower isoprene concentration than the converted RO₂ signal for isoprene in the bottom panel.

The upper panel in figure 3 has been incorrectly labelled as the OH decay in the presence of isoprene, when in fact, this decay was taken in the absence of reagents; the reactivity determined from the exponential decay is $\sim 25 \text{ s}^{-1}$. We apologise for the obvious confusion this error has caused.

Does the FAGE OH signal in the bottom panel includes signal from both unreacted OH and converted RO₂?

As discussed in the responses to referee 1: Considering isoprene, at a typical concentration of 1×10^{13} molecule cm⁻³ as used in the experiments, we can estimate a pseudo-first-order rate of removal of OH of $> 1000 \text{ s}^{-1}$, and so the lifetime of OH is $< 10^{-3} \text{ s}$; this compares to the residence time in the flow tube before sampling by FAGE of $\sim 4 \text{ s}$. So we do not expect any OH to remain and the signal displayed in the bottom panel of Figure 3 may be attributed solely to converted RO₂.

If so, why is the FAGE OH signal for the alkanes lower than the initial OH signal?

Please refer to the discussion above

The paper would benefit from additional information and clarification of how the data in these experiments were used to extract the RO₂->OH conversion efficiencies. Did the authors model the production and loss of the different RO₂ radicals in the flow tube?

The confusion relating to the approach for determining the OH yields from RO₂ radicals in the time-resolved experiments is caused by the incorrect labelling of Figure 3. This will be rectified in the revised manuscript and this, along with further discussion on radical lifetimes in the flow tube, should clarify our experimental approach.

3) In Figure 6, the authors demonstrate that reducing the concentration of NO can reduce the RO₂-> OH conversion efficiency. However, it is not clear which FAGE axis

design and reaction time corresponds to the measurements/model. Is this the FAGE cell with 10 ms of reaction time used in the time dependent radical source experiments, or the field FAGE cell with 1 ms of reaction time? Given that there are mixing issues associated with injection of NO for each FAGE cell, the authors should demonstrate that the field FAGE cells are able to minimize (and maximize as a measure of alkene and aromatic RO₂) the RO₂ interference.

We used detection cell A for these experiments which is the primary FAGE cell used for ambient observations and so have demonstrated that we can minimise the interference in the field. This will be clarified in the revised manuscript.

We would like to highlight that the model predicted HO₂:RO₂ ratio vs [NO] is not totally consistent with the ratio observed experimentally. We found, as displayed in figure 6, that the observed ratio does not increase as rapidly as the model predicts as [NO] decreases. This, in effect, means we observe an enhanced RO₂ → OH conversion relative to HO₂ → OH conversion (most apparent at the lowest [NO]), suggesting that HO₂ may be being preferentially lost in the cell relative to RO₂ radicals. This may be caused by more efficient removal of HO₂ relative to RO₂ by H₂O clusters (Creasey et al., 2001). This finding further highlights the need to experimentally determine the level of interference for each specific FAGE system and specific conditions.

4) The authors attempt to summarize the impact of the interference on their previous measurements in section 4.3. It would be helpful to summarize this information in a Table that includes the campaign, a reference to the original analysis, the original model/measurement agreement for HO₂, which FAGE cell was used, the average alkene/alkane RO₂ conversion efficiency from this paper, and the impact of the interference on the previous conclusions.

We agree that a table, as suggested, would act as a useful reference. We will supply information regarding the extent of model-measurement agreement for HO₂ for the earlier campaigns and the detection cell used. We only have limited information, however, on the modelled RO₂ speciation which would be needed to calculate the impact of the interference absolutely. We would also not be confident that we could determine the RO₂ conversion efficiency that should be applied for some of the earliest campaigns without a reasonable degree of uncertainty. For example, during EASE96, 97 and AEROBIC several hundred sccm of nitric oxide were added to the detection cell used (which was most similar to Cell A described in the paper, although not identical) yet only poor conversion of HO₂ to OH was achieved (10% conversion) suggesting that the mixing of NO into the ambient air stream was extremely poor or as suggested by Creasey et al. (2001) could indicate that HO₂ was efficiently removed within the cell by H₂O clusters that formed in the low pressure expansion region. Without recreating the exact conditions and conducting interference tests on the early FAGE systems, we are unable to put absolute values on the extent that HO₂ concentrations may have been affected.

5) In Figure 7, the authors illustrate the ability of one FAGE axis (cell a) to selectively detect HO₂ (at low added NO) and alkene/aromatic/long chain aliphatic derived RO₂ (at high added NO) and compare it with the measured total RO₂ using FAGE cell (c). The authors should clarify whether the concentrations shown in this Figure are derived from Equations 7 and 8, or whether these are the results of the different measurements modes, where the HO₂ concentrations are the measurements from cell (a) at low added NO, the alkene/aromatic/long chain aliphatic RO₂ concentrations are the measurements from cell (a) at high added NO (with the measured HO₂ concentrations subtracted), and the aliphatic RO₂ are the measurements from cell (c) with the high NO measurements from cell (a) subtracted. In either case, it would be useful to include the measured total RO₂, HO₂^{*}, and HO₂ to help clarify what is actually measured and what is derived from the individual measurements.

To clarify, the [HO₂] (red) and [RO₂i] (mustard) have been derived using Equation 7 and 8 (i.e. from HO₂* signal observed when using cell A at high and low NO flows; with the sensitivity to HO₂ and RO₂i determined experimentally at the two NO flows used). The C1-C3 alkane-derived [RO₂] (green) was determined from Cell C detection of total [RO_x] with the derived [HO₂] and [RO₂i] subtracted. This will be made clearer in the revised manuscript.

References:

Creasey, D. J., Heard, D. E., and Lee, J. D.: OH and HO₂ measurements in a forested region of north-western Greece, *Atmos Environ*, 35, 4713-4724, Doi 10.1016/S1352-2310(01)00090-5, 2001.

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, *Phys Chem Chem Phys*, 11, 5935-5939, Doi 10.1039/B908511d, 2009.