**Atmospheric
Measurement
Techniques**
Discussions

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Interactive comment on "Reporting the sensitivity of Laser Induced Fluorescence instruments used for HO$_2$ detection to an interference from RO$_2$ radicals and introducing a novel approach that enables HO$_2$ and certain RO$_2$ types to be selectively measured" *by* L. K. Whalley et al.

Anonymous Referee #1

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The authors report the investigation of the measurement sensitivity of an instrument for the detection of atmospheric HO$_2$ applying laser-induced fluorescence (LIF). This is an important work because of recently discovered interferences from RO$_2$ radicals. Since the magnitude of this interference is specific for every instrument, this work gives new information about the HO$_2$ measurements done by this group in the past and consequences for measurements in the future. Furthermore, the authors develop an ap-

proach utilizing this interference, in order to estimate the concentration of certain RO$_2$ 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 RO$_2$ 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 RO$_2$ 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 HO$_2$ 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? (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? (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? (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. (5) Please give numbers for the loss rate of OH and HO$_2$ 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? (6) In Fig. 3 an OH decay curve in the presence of isoprene is presented, which indicates that OH is converted to RO$_2$ on a similar time scale as the HO$_2$ and RO$_2$ 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. (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.

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 extend 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?

Separation of total RO_2 and "interfering" RO_2: The authors show an approach to separate between HO_2, total RO_2, and specific RO_2, which causes interferences in the HO_2. 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 RO_2 species. In Eq. 7,8 it is assumed that the conversion efficiency in the HO_2 is the same for a group of certain RO_2 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 RO_2 distribution, in order to calculate HO_2 and RO_2 concentrations. For specific conditions with only few RO_2 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 HO_2* is taken from model calculations for the two different measurement modes (NO concentrations) of the HO_X

detection cell. I would recommend to discuss the limitations of this approach in Section 4.2 in more detail.

Figure 6: The ratio of the HO_2 to RO_2 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.

Technical points:

p6258 l5: There is one right parenthesis more than needed after "Leybold"

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.

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.

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

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

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.

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

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