

## Answer to Anonymous Referee #2

### General Comments

The present study provides an intercomparison exercise on the measurement of peroxy radical during the AMMA campaign. In this intercomparison exercise, a LIF-FAGE instrument and two similar instruments based on the peroxy radical chemical amplification were subject to a blind intercomparison. Because the intercomparison was performed under real airborne conditions, it is very useful in order to identify biases and artefacts of these instruments. In this sense, this paper is very interesting and is in the scope of ACP. However, some discussions should be developed to explain the discrepancies observed between the measurements or between the measurements and the model. Moreover it appears that this paper may have been submitted “too early” since some information which are necessary to evaluate the accuracy of the instruments and the model are not available actually and are presented in papers “in preparation”. Moreover, some instruments such as the radiometers have to be recalibrated to provide more accurate photolysis rates. In consequence, the authors are encouraged to develop some technical details in this paper.

### 2. Experimental description

- Both detection limits and estimated accuracies have to be given for all 3 techniques which is not the case actually. Moreover, errors bars should be added on Figure 2 for all data to allow relevant comparisons of the concentrations measured by the different instruments. So errors bars for HO<sub>2</sub> and RO<sub>2</sub>-BAe should be added.

The manuscript quotes the LOD for FAGE as 0.31pptv on P8457 L9. The total uncertainty of the measurement is 26 % at 2 $\sigma$ . The error bars have been added to the data.

Concerning the PERCA 4, the accuracy of the measurement is stated as of the order 40% in the current text. In fact, the value determined from the calibration of the PERCA 4 is 37%; this value can be used to derive percentage error bars for each measurement data point. The average detection limit determined over the intercomparison period is 10.4 pptv for a 60 s averaging interval.

The following sentence is added to the end of section 2.1.2 to satisfy the referee comments:

*“The average detection limit of the PERCA 4 dual channel measurement over the intercomparison run at 697 hPa is 10.4 pptV for a 60 s averaging interval.”*

- In the FAGE instrument description, it is explained that the instrument and associated calibrations are described in detail in an another paper but this last one is in preparation actually. In consequence, technical details on this instrument are not available now. This is a real limitation to evaluate the accuracy of the measurements and to compare the results with those obtained by other instruments and by the model. Therefore, more information on the calibrations, the rescanning process of the laser and the estimated accuracy has to be given here.

The cited manuscript was published in ACPD days before the present manuscript and the corresponding reference was accordingly updated for the interactive discussion: Commane, R., Floquet, C. F. A., Ingham, T., Heard, D. E., Stone, D. and Evans, M. J.: Observation of OH and HO<sub>2</sub> Radicals over West Africa, Atmos. Chem. Phys. Discuss., 10, 7265-7322, 2010. In the meantime the paper has been revised and published in ACP: Atmos. Chem. Phys., 10, 8783–8801, 2010, doi:10.5194/acp-10-8783-2010. The corresponding reference has been updated.

### 3. Supporting calculation or modelling

- As in the experimental section, full details on the modelling exercise are given in another paper which is in preparation. So the authors are encouraged to find a solution to provide more information on the model.

The cited manuscript has already been published in ACPD: HO<sub>x</sub> observations over West Africa during AMMA: impact of isoprene and NO<sub>x</sub>, D. Stone, M. J. Evans, R. Commane, T. Ingham, C. F. A. Floquet, J. B. McQuaid, D. M. Brookes, P. S. Monks, R. Purvis, J. Hamilton, J. Hopkins, J. Lee, A. C. Lewis, D. Stewart, J. Murphy, G. Mills, D. Oram, C. E. Reeves, and D. E. Heard, Atmos. Chem. Phys. Discuss., 10, 17029-17072, 2010

- Moreover, several VOCs have been measured during the intercomparison exercise and are used to estimate RO<sub>2</sub> and HO<sub>2</sub> concentrations. They are mainly alkanes, alkenes and oxygenates (in particular secondary oxygenated products arising from the degradation of isoprene). However, one can wonder about the presence of other VOCs in the air mass, in particular of other biogenic and/or

anthropogenic species (benzene, toluene, . . .). Are these missing VOCs supposed to be significant in the probed air masses ? Since other measurements of VOCs were performed during AMMA campaign aboard other planes or at the ground, could the authors use these information to estimate if some missing organic compounds induce a significant error on the simulated concentrations of RO<sub>2</sub> and HO<sub>2</sub> ?

Every model will have 'missing' VOCs as we can never hope to measure every species present in the atmosphere. Using data from other planes and from ground based measurements will introduce so much more uncertainty in the model that any results it would give would be rather meaningless. In addition, the chemistry is dominated to a fairly large extent by isoprene and measured VOCs and individual contributions from other species would be therefore small. There was virtually no difference in the model output when including benzene and toluene measured on the BAe-146 in test runs. In Stone et al., 2010 the model sensitivity to monoterpenes is discussed. The results indicate that for a set of reactive species the model is relatively insensitive and the model covers the dominant radical production and loss processes.

On page 8458 line 23 the text has been extended as follows: *“There was virtually no difference in the model output when including benzene and toluene measured on the BAe-146 in test runs. The results indicate that for a set of reactive species the model is relatively insensitive and the model covers the dominant radical production and loss processes.”*

**- p.9 first paragraph, replace NO<sub>x</sub> by NO<sub>y</sub>.**

It has been replaced

**- TUV : give a reference.**

TUV can be referenced to <http://cprm.acd.ucar.edu/Models/TUV/> This reference has been included in the text on page 8459 line 12.

**. Discussion of results**

**- p9 and 10 : At the second pressure level, abrupt changes in the concentration of HO<sub>2</sub> have been observed at 15:35 and 15:42. Both of these steps follow periods where the laser wavelength was rescanned. The authors indicate that there not evidence to suggest that the sensitivity of the instrument has changed and conclude that these changes are real variations of [HO<sub>2</sub>]. However, this explanation is not very clear and should be developed. Indeed, this is quite surprising that these abrupt changes occur exactly at the time where the laser was rescanned ! Moreover, this decrease in the HO<sub>2</sub> concentration is not correlated to a decrease of RO<sub>2</sub><sup>\*</sup> concentration (a slight increase of [RO<sub>2</sub><sup>\*</sup>] was observed between 15:30 and 15:35) and is not simulated by the model. In conclusion, the authors should provide a more clear and justified explanation of these changes.**

In P8460 L24 the following text have been included for clarification: *“..... are real variations. It can be demonstrated that the observed [HO<sub>2</sub>] is directly and linearly proportional to the excitation laser power which is monitored at 1 Hz during ambient measurements and used to normalize the observed signal. This normalization procedure has been applied to the data in question. The relationship between the observed [HO<sub>2</sub>] and excitation wavelength is non-linear and is an integration of the laser wavelength and line width and the OH rotational line width. A confirmation that the laser wavelength was centered on the OH rotational line throughout this period before and after the rescanning process is obtained by monitoring the signal produced in the OH reference cell in which a high and very stable [OH] (produced by the thermolysis of water vapour) is probed by a measured laser power. The signal obtained from the reference cell during the period where the steps in ambient [HO<sub>2</sub>] were observed was stable. The additional factor which affects the observed [HO<sub>2</sub>] is the flow rate of NO into the detection cell, and again the relationship is non-linear, but the flow of NO is controlled and measured by used of a thermal mass flow controller and during this ambient measurement period the flow was at the set point value of 10.0 sccm. Therefore there is no indication of any systematic variation in instrument sensitivity to HO<sub>2</sub> in this period.”*

- Photolysis rate are of prime importance to model the concentrations of HO<sub>2</sub> and RO<sub>2</sub>. However, systematic differences of about 25% have been observed between the radiometers aboard the two aircrafts. Calibrations are in preparation to clarify the origin of these discrepancies but results of these calibration would be really useful for this paper. So, the authors should add the results of these calibration, if possible.

The calibrations of the D-Falcon radiometers carried out recently confirmed the previous calibration factors used previously. These agree within 6% and 1% for the upward and downward facing radiometers respectively. The text on pages 8461 (section 4) and 8468 (conclusion) has been correspondingly enlarged for clarification:

*“ $j(O^1D)$  was not measured on board the D-Falcon. At 697 hPa, a systematical difference between  $j(NO_2)$  radiometers on both aircrafts was identified (see Fig. 7). While the downward facing  $j(NO_2)$  radiometers show very good agreement (within 6%), the D-Falcon upward  $j(NO_2)$  radiometer is about 25-35% systematically higher than the BAe -146 upward facing sensor at both pressure levels. According to Volz-Thomas et al., (1996), temperature variations between 25 and -40°C can only account for 2-3% changing in the instrument sensitivity. The calibrations of the upper and lower  $j(NO_2)$  radiometers in the BAe-146 before and after AMMA are consistent with one another having both been referenced to the Tropospheric Ultraviolet and Visible radiation model (TUV, <<http://cprm.acd.ucar.edu/Models/TUV/>>). Calibrations of the D\_Falcon sensors carried out before and after the AMMA campaign show little variance (6%). The downward facing radiometers are mainly exposed to indirect diffuse radiation while the upward facing radiometers get both, direct and diffuse radiation. As a consequence, upward looking radiometers have an additional uncertainty due to the azimuth and zenith dependence of the radiometer sensitivity. Previous investigation has shown that the total combined accuracy of the D\_Falcon upward looking radiometer is 14% and of the downward looking radiometer is 3.3%. If both radiometers are subject to similar errors, it is reasonable that the upward facing  $j(NO_2)$  measurements, with lower accuracy, show a larger difference within the combined total errors, than the downward facing radiometers. Differences in the surface reflectivity around the sensors in each aircraft may also affect the result.”*

On page 8468:

*“b) The response of the  $j(NO_2)$  radiometer on board the D-Falcon remains systematically higher than the equivalent radiometer on the BAe-146. This is the result of the 25-35% difference observed in the upward facing sensors at both pressure levels. This difference remains within the combined total errors of both radiometers which is mainly related to the azimuth and zenith dependence of the sensitivity of upward facing radiometers. This emphasises....”*

The Figure 3 (in the revised manuscript version Figure 7) has been however updated with the new calibration factors.