<h1 style="text-align:center">Answer to Anonymous Referee #1</h1>

General comments.
The article presents the measurements of the peroxy radicals, RO2 and HO2, over West Africa during WAM. These data may be significant for the understanding of photochemistry under conditions of African Monsoon. Hence, the article is definitely in the scope of the ACP. To be useful for the analysis of the related atmospheric processes it is necessary to have a clear understanding of the peroxy radical measurements' accuracy and uncertainties. In this respect the presented results are of a great interest because the measurements using two different chemical amplifier instruments are presented. As a significant disagreement between these measurements has been observed, the analysis of these intercomparison data may provide information important for the estimation of the present uncertainties associated with airborne implementation of the PERCA technique. However, the description of the instruments and of their calibration/characterisation procedures presented in the article, as well as the presented discussion of the observed discrepancy, does not allow to make any clear conclusions about the instrument's performance and about the source of the discrepancy. It is desirable, that in the final version of the article the authors provide more clear and detailed explanation/discussion of the observed disagreement between the two instruments

I) Instruments' description
To make any sense of the presented intercomparison measurements, a clear description of the main instrument characteristics should be presented. While the description of the DUALER can be found in the literature, the description of the PERCA IV is not available. (In the cited article of Green et al., 2006 only ground based instrument is described, while the PhD thesis of D. Brookes with a description of the instrument characterisation is not easily available.)

I.1) Provide the description of the airborne version of the PERCA IV instrument including the inlet and reactors characteristics, inlet flow rates, conditions in the reactor during the flight, concentrations of reactants, etc.. Also, describe briefly calibration procedure accounting for the dependence of the instrument performance (CL, NO2 detector, inlet losses, . . .) on pressure and temperature.

The instrument described by Green (2006) is the PERCA 4 instrument, in that PERCA 4 represents the development of a dual channel instrument jointly by the University of Leicester and the University of East Anglia. The subsystems and principle of operation of the current PERCA 4 instrument and that described by Green (2006) are essentially the same except changes have been made in components and their layout to suit operation on the BAe-146.

The fundamental difference between the PERCA 4 instrument and the DUALER instrument is related to the inlet design, sampling and calibration methods. In the absence of another published description of the PERCA 4 instrument and with the emphasis of the paper on the description of the measurements we have focused on the fundamental differences in the instrument design, operation and calibration as appropriate for this paper.

The PhD thesis that gives the details is publicly available from the University of Leicester, Leicester Research Archive (https://lra.le.ac.uk/). This citation should be sufficient for further detail if required, if the primary differences in the measurements are established in the paper.

To this end the following changes (in red) have been made to the section 2.1.2 description of PERCA 4:

"The University of Leicester airborne PeRCA instrument (designated PERCA 4) is a dual channel (two inlet, two detector) PeRCA and was operated on board the BAe-146 during AMMA. The PERCA 4 instrument was originally designed and built jointly between the University of Leicester and the University of East Anglia. The application of the PERCA 4 dual channel system to ground based measurements was first described by Green et al. (2006). The aircraft instrument, its characterisation, calibration procedures and performance during the measurement campaign are detailed in Brookes (2009).

PERCA 4 uses two equivalent channels each comprising a low-volume pyrex inlet coupled to a modified LMA-3 Scintrex NO_2 detector channel. A sample flow of 2 slpm is drawn through each inlet inclusive of ambient air and reagent gases. In each inlet the chain chemistry described in Sect. 2.1 is modulated between chain amplification mode and background measurement mode by switching the addition of a flow of the reagent CO (100 sccm, 5%/vol. equivalent in the sample flow) with an identical flow of N_2 between the front and back of the inlet (typically every 60 s) while a flow of the reagent NO (10 sccm, 3 ppmV equivalent in the sample flow) is added continuously at the front of the inlet. Reagents and N_2 are

supplied under pressure from gas cylinders held within the instrument rack inside the aircraft cabin with flow control maintained using mass flow controllers (Tylan FC260, now manufactured and distributed by Celerity Inc.). Total sample flow is maintained at 2 slpm (1.79 slpm ambient air, 0.21 slpm reagent gases) by a combination of mass flow meters (MFM, Tylan FM360) in series with stepper motor controlled needle valves; active control of the stepper motors via computer software provides sample flows to within ±50 sccm. A Leybold Sogevac SV16 oil filled rotary vacuum pump (capable of a pumping speed of 14.5 m^3h^{-1}, down to a pressure of 80 mbar) provides suction to pull the sample air flow from the inlets through to the Scintrex detectors. The channels are run out of phase as shown in Fig. 2, to provide simultaneous measurements of chain amplified and background NO_2, and the radical chain amplified NO_2 signal is determined by subtraction of the background measurement."
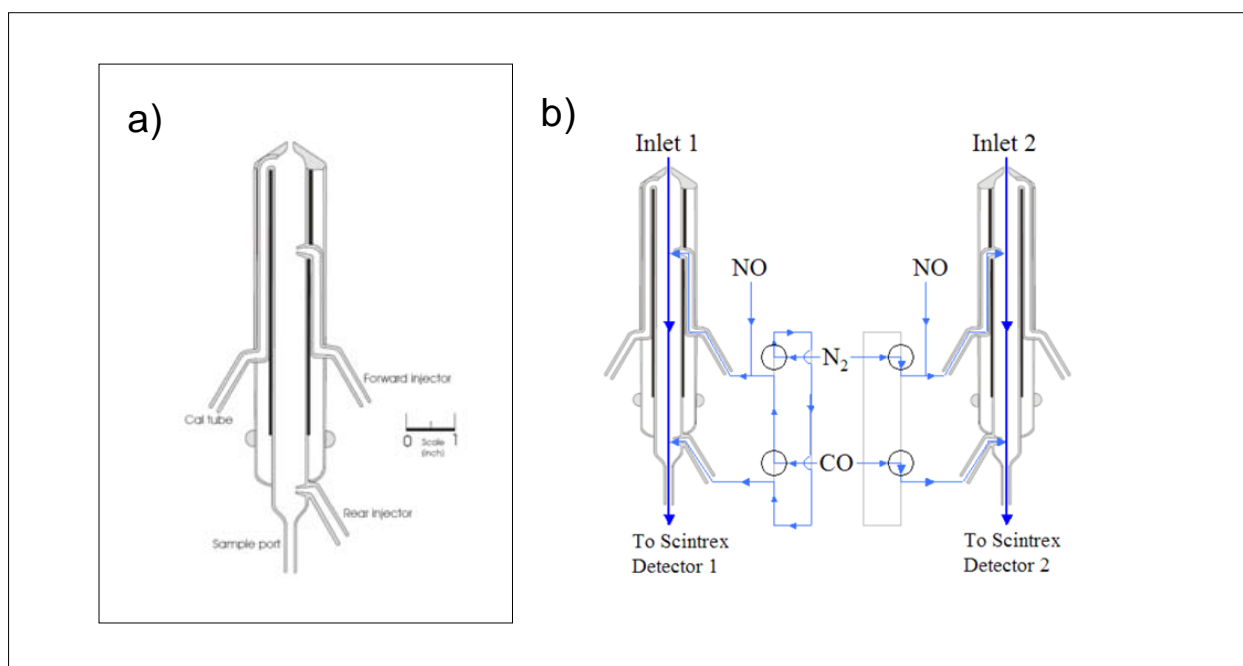

Fig. 2. a) Scale diagram of aircraft inlet and b) PERCA 4 dual inlet scheme: Inlet 1 in chain amplification mode (NO and CO addition at front port, N_2 at back), Inlet 2 in background measurement mode (NO and N_2 addition at front port, CO at back), arrows indicate direction of gas flow, circles indicate 2-way valves (from Brookes, 2009).

It was not possible to perform in flight CL calibrations on board the BAe-146, and consequently calibrations were performed at ground level in the laboratory following the AMMA campaign. The calibration procedure for the PERCA 4 inlet chain lengths is based on the method of Clemitshaw et al. (1997), whereby known concentrations of methyl peroxy are generated through UV photolysis of methyl iodide. The calibration procedure as yet does not take into account the change in CL with temperature and pressure although it would be preferable to perform CL calibrations at different altitudes, to account for the temperature and pressure dependent rate constants of the chain chemistry reactions.

The PERCA 4 inlets sample the airflow directly through the aircraft wall perpendicular to the aircraft direction of flight. The inlets can be heated to reduce the impact of humidity on the CL; however this system fails in flight on the BAe-146. The result is that for the PERCA 4 instrument the air temperature, pressure and humidity were expected to remain at ambient levels on sampling and impact on the CL. A systematic reduction in the chain length with altitude has been modelled (Brookes, 2009) using the FACSIMILE package (v4.40.101, MCPA Software Ltd.) using an inlet chemistry reaction mechanism based on that of Hastie et al. (1991) and rate coefficients taken from the recommendations of Sander et al. (2006) and Atkinson et al. (2004, 2006). Pressure and temperature were constrained in the model using the pressure and temperature altitude profiles measured from the BAe-146 during AMMA, further details of the model setup can be found in Brookes (2009). At the altitude of the intercomparison level run where the PERCA 4 operated (700 mbar) a reduction in the CL of the order 20% is modelled. The reduction of the PERCA 4 chain length with altitude will contribute to systematic bias between the PERCA 4 and DUALER measurements, where the DUALER reactor is pressure controlled and the PERCA 4 chain length has not been corrected. The modelled variation in the CL at altitude (CL_{alt}) relative to the CL at ground level (CL_0) is shown as a function of pressure in Fig. 3.
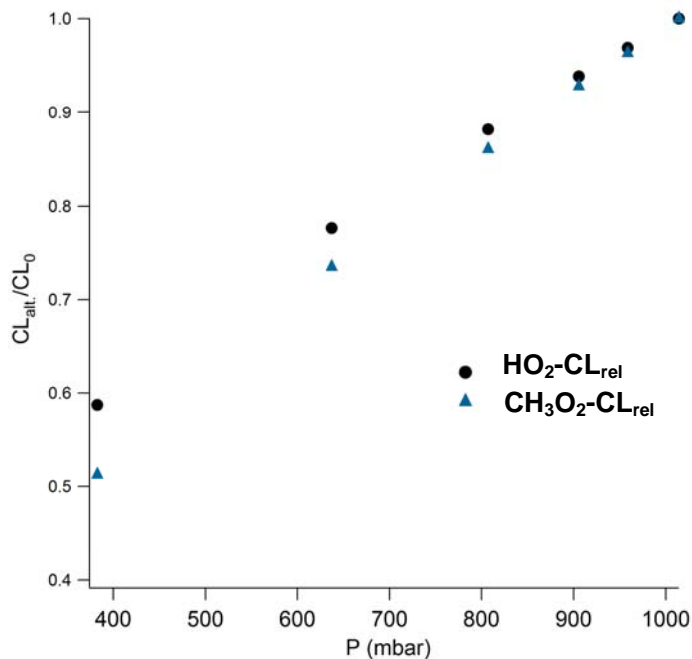
Fig.3. Modelled variation in the chain length relative to ground level (CL$_0$) for HO$_2$ and CH$_3$O$_2$, CL$_{alt}$ stands for CL at single altitude (Brookes, 2009)

Concerning the detector calibration, following text has been included on page 8456 line 15:

"The calibration procedure for the NO$_2$ sensitivity of the LMA-3 Scintrex detectors is detailed in Brookes (2009). Ordinarily the LMA-3 detectors are calibrated by mixing the output from a VICI Metronics NO$_2$ wafer permeation device with varying flows of zero air, but owing to technical problems with the calibration system on board the BAe-146, it was not possible to perform reliable in-flight calibrations. An alternative method was developed using the background signal on the LMA-3 detectors along with the in-situ ozone measurements made on board the BAe-146 with a commercial Thermo Environmental Instruments Inc. 49C ozone analyser. The relative levels of ozone and NO$_2$ encountered during AMMA were such that the background signals measured on the LMA-3 detectors were almost entirely due to the oxidation of reagent NO by ozone with a negligible contribution from ambient NO$_2$. The absolute NO$_2$ background concentration generated from this reaction was derived using the temperature dependence of the reaction rate constant and the variation of the residence time with temperature and pressure. The derived background NO$_2$ concentration within the sample flow was used to weight the detector response. Thus the NO$_2$ sensitivity of the detectors was calculated along the flight track for every point during which ozone measurements were available."

II) Dependence on humidity.
II.1) It is claimed that the observed discrepancy is explained by the problems related to the humidity correction. Provide the graph showing the temperature, humidity and corrections under these conditions during the flight.

The calibration data for the aircraft inlet CL variation as a function of relative humidity along with the curve fit used to parameterize the correction factor of the PERCA 4 is shown here for further information:
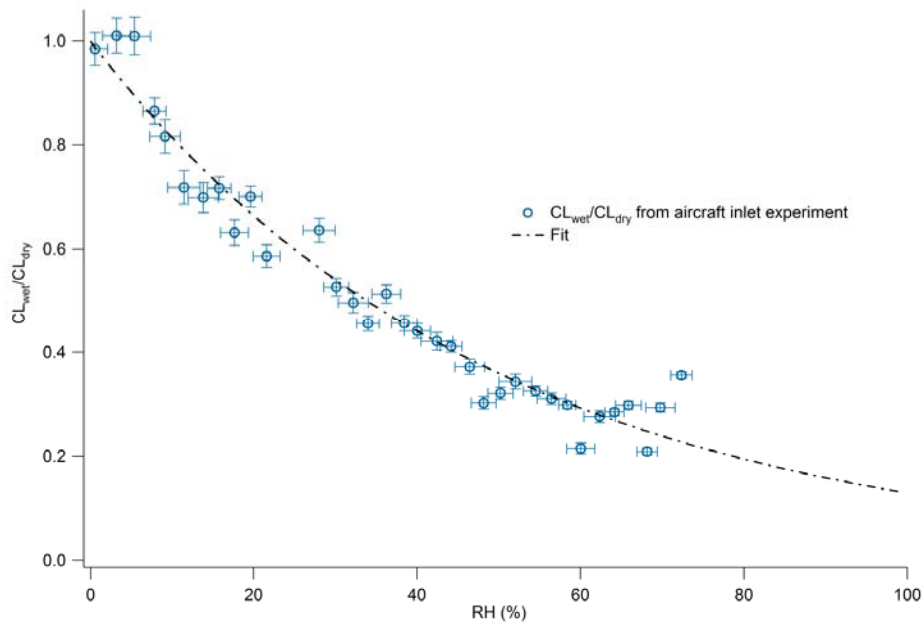
Figure – University of Leicester PERCA 4 aircraft inlet chain length humidity dependence – Relative change in the chain length with relative humidity (%)

The text has been extended (in red) on page 8455 line 13:

"To correct for the humidity interference to the chain chemistry a correction function (dependent on relative humidity) was derived and applied to the AMMA PERCA 4 [RO$_2$] dataset (Brookes, 2009). On application of the correction to the AMMA dataset as a whole the concentrations scaled on average by a factor of 4.4 resulting in up to several hundreds of pptv [RO$_2$] (Brookes, 2009); this scaling is considered unrealistic since concentrations this high have not been reported in the tropical troposphere. By comparison of the uncorrected PERCA 4 [RO$_2$] dataset to output from the DSMACC model (Emmerson and Evans, 2009; Stone et al., 2010), the uncorrected data was assessed for any systematic bias with humidity (Brookes, 2009). The model to measurement ratio exhibits no trend with relative humidity as demonstrated in Fig. 4, and thus it is believed to be inappropriate to apply the humidity correction to this dataset and therefore the intercomparison was made using the uncorrected data.*
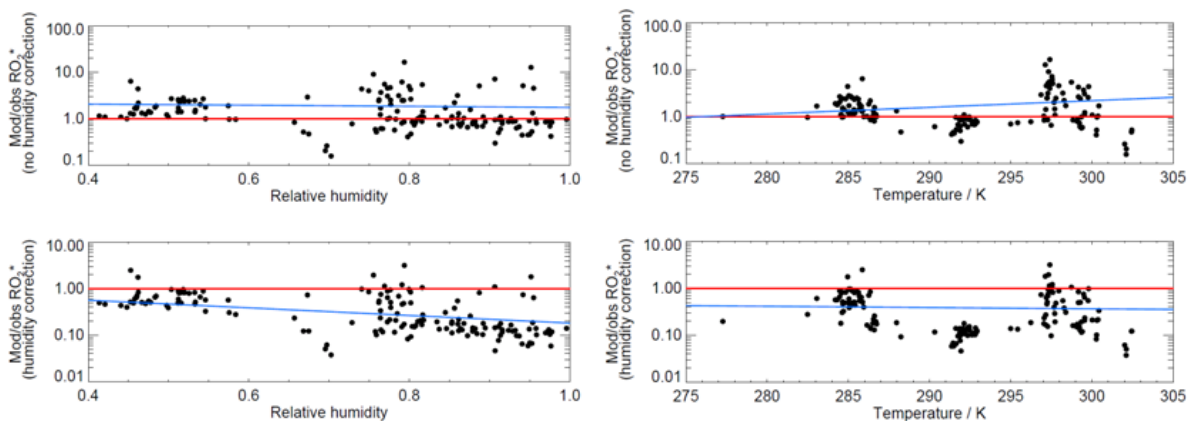

Fig.4. DSMACC model to PERCA 4 measurement ratio as a function of a) relative humidity (as a fraction), and b) temperature (in Kelvin).

The expected humidity bias in the measurement response was not observed in the PERCA 4 AMMA dataset despite the consistently high humidity encountered during the monsoon season (Brookes, 2009), and thus a potential explanation is sought. Owing to their low thermal mass the PERCA 4 inlets are expected to be in thermal equilibrium with the aircraft cabin and ambient airflow. A temperature gradient is also expected between the inlet tip in contact with the ambient airflow, and the inside in contact with the aircraft cabin. The most significant interaction between the inlet and the ambient airflow will occur on sampling and it is hypothesized that at this cold point water vapour may condense, thus reducing the

relative humidity sampled. This hypothesis also provides an explanation of the observed loss of sample flow through the mechanism of inlet tip icing; the sample flow was observed to drop dramatically at altitudes above the freezing point in highly saturated conditions during AMMA (Brookes, 2009). "

On page 8460 line 2 (section 4: discussions of results), following text and figure have been additionally added (in red):

"*As explained in Sect. 2.2.2, a relative humidity correction was applied for…….concentrations. Fig. 6 illustrates the loss in PERCA 4 sample flow during the intercomparison flight. With the aircraft ascending to higher altitude the temperature falls below freezing and simultaneously the water content changes from a mixed phase to condensed water (ice) only, as indicated by the Nevzorov probe data from the BAe-146. The simultaneous drop in sample flow with a phase change in water is seen to indicate condensation followed by freezing occurs, which then blocks the sample flow to the inlet. The combination of the ambient temperature dropping below freezing and elevated ice content coincident to a drop in sample flow is common in all AMMA flights where the PERCA 4 instrument was operational on board the BAe-146. There has as yet been no experimental verification to quantify the level of humidity within the inlet in flight.*"
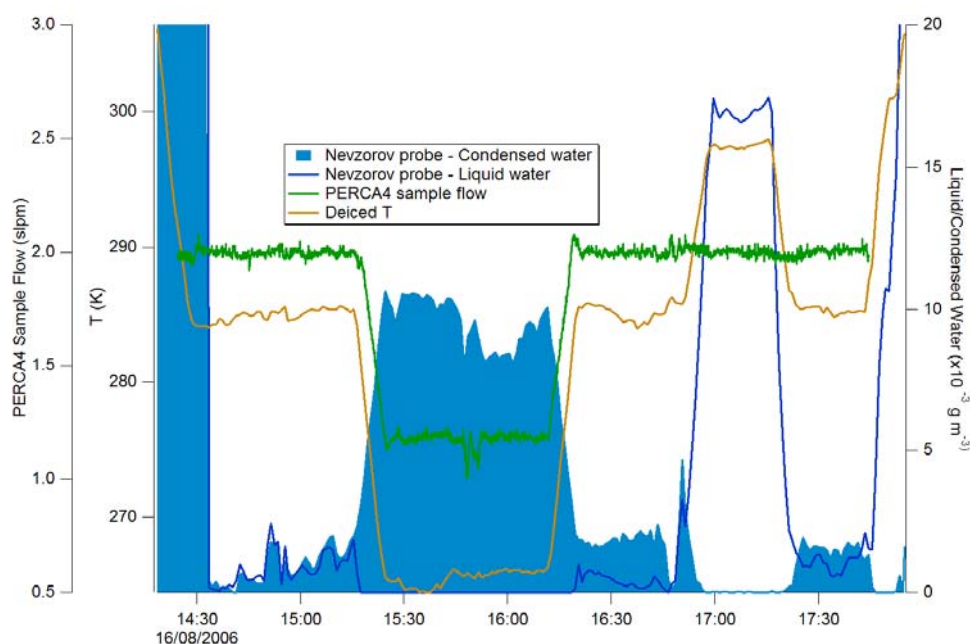

Fig.6: Time series of PERCA 4 sample flow, with temperature and water content during the intercomparison flight

DUALER II.2) It is stated that the humidity correction was not important for the DUALER. Please be more specific and give the value of the correction under the flight conditions. Have you measured the dependence of the DUALER CL on the humidity at low temperature? Can you estimate the temperature in the reactor? If the humidity dependence is due to the HNO_3 formation in the reaction of HO_2 with NO, the effect can be more important at low temperature. The influence of the humidity can not be neglected on the basis of the arguments given in the article.

As stated in the text (end on page 8453 and 8454) the inner part of the DUALER inlet and therefore the outer part of the reactors was connected to the cabin of the aircraft and as a consequence, the temperature of the reactors was always higher than the temperature of the sampled air.
This temperature was regularly controlled and documented and remained above 0°C under all conditions (see plot below).

$$y = -0.0007x^2 + 0.2517x + 14.332$$
$$R^2 = 0.9087$$
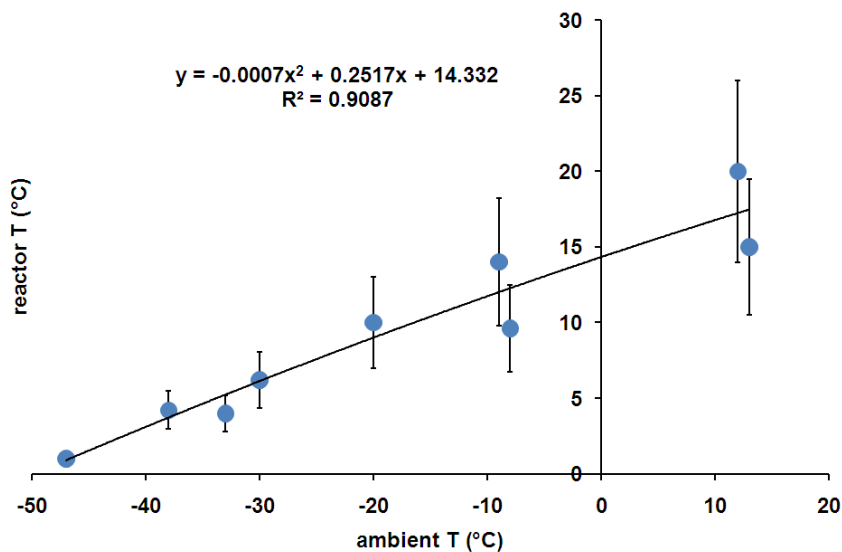
The relative humidity is defined as $RH = P^{HO2}_{partial} / P^{HO2}_{saturation}$. At pressures below 700 mbar, the difference in temperature between ambient air and reactors is high and the increase in $P^{HO2}_{saturation}$ in the reactors dominates the RH decrease. At lower altitudes, i.e., higher pressures, the decrease in the RH relative to the ambient is dominated by the decrease in the $P^{HO2}_{partial}$ as the DUALER operates at 200-300 mbar. During the intercomparison exercise the latter effect dominated and the RH in the reactors remained below 15%. As the effective CL of the DUALER reactor is dominated by the wall losses in the pre-chamber, the effect of the RH in the reactors was considered to be within the error of the CL determination.

Laboratory investigations (Reichert et al., 2000) at 1000 mbar show no significant difference in the RH dependency of the chain length between 20° and 30°C and at the ambient temperatures dominating during the intercomparison exercise (around 15°C) a similar behaviour is expected. Mihele and Hastie (2000) showed that the RH dependency of the CL in their reactor decreases at low temperatures. We are presently investigating the variation of the CL dependency on the RH with the pressure but also expect a decrease of the RH effect at lower pressures.

On page 8454 line 6 the text has been extended as follows:

"....reactors (Kartal, 2009). During the intercomparison exercise the decrease in the RH relative to the ambient was dominated by the decrease in the $P^{HO2}_{partial}$ as the DUALER operated at 300 mbar. The RH in the reactors remained below 15%. At 300 mbar this effect in the CL is expected to be within the error of the CL determination."

PERCA IV
II.3) Agreement with the model (Fig.6) is better for the BAE data with applied humidity correction. Explain why you consider that the correction results in "unrealistically" high RO2.

General comments in response:

We do not agree that model-measurement agreement is better for the PERCA 4 data with humidity correction applied (see e.g. Fig. 4). In Figure 6 (in the present revised manuscript figure 10) the PERCA 4 RO_2^* concentration is approximately half the model RO_2^* concentration while the correction factor has a mean value of 2.83 over the period 15:00-15:18 UTC.

It is understandable for the calibrated measurement to underestimate the total concentration owing to sampling loss of HO_2, the measurement responding with varying efficiency dependent on the population of peroxy radicals sampled and the modelled reduction in the chain length at altitude with respect to the applied chain length derived under approximately STP conditions in the laboratory.

Accounting for the chain length altitude dependence (scaling up by ~20% as stated in Section 2.1.2) would bring the non-humidity corrected data closer to the DUALER measurement. The chain length is not corrected for the altitude since the modelled dependence has not been experimentally verified; the intercomparison provides some verification of the modelled dependence from the scaling between the

DUALER and PERCA 4 data. A similar modelled trend has been experimentally validated for the DUALER instrument (Fig. 4 in Kartal et al., ACP, 10, p3047, 2010).

Multiplying the PERCA 4 data by a factor of ~3 to correct for the ambient relative humidity inflates the "measured" concentrations to greater than that modelled or that measured by a comparable instrument. We consider the humidity corrected data "unrealistic" based on data from the whole campaign and not this period of this flight alone. The correction scales data by a factor of ~4.4 on average resulting in up to several hundreds of pptv RO_2^*. This scaling is therefore considered unrealistic since we do not know of any reported occurrence of concentrations this high in the atmosphere.

II.4) The arguments based on the comparison of the model and measurements are not convincing. According to Fig.2, the correction factor was approximately the same for all the data set. So, how could any trend between the humidity (apparently unchanged during the flight) and the model to measurements ratio be observed? Please present a Figure showing the humidity, temperature and the model to measurements ratio.

Figure 2 (in the present revised manuscript figure 5) plots the "humidity corrected" data alongside the non-corrected data for the intercomparison period alone. The PERCA 4 instrument operated over a period of several weeks, on a number of flights under varied conditions and absolutely no trend was observed in the model to "non corrected" measurement ratio as a function of relative humidity. The "humidity corrected" measurement data consistently exceeds the model with the level of disagreement increasing with relative humidity as the correction factor increases. This is demonstrated in Fig. 4, included in the revised manuscript and reproduced here.
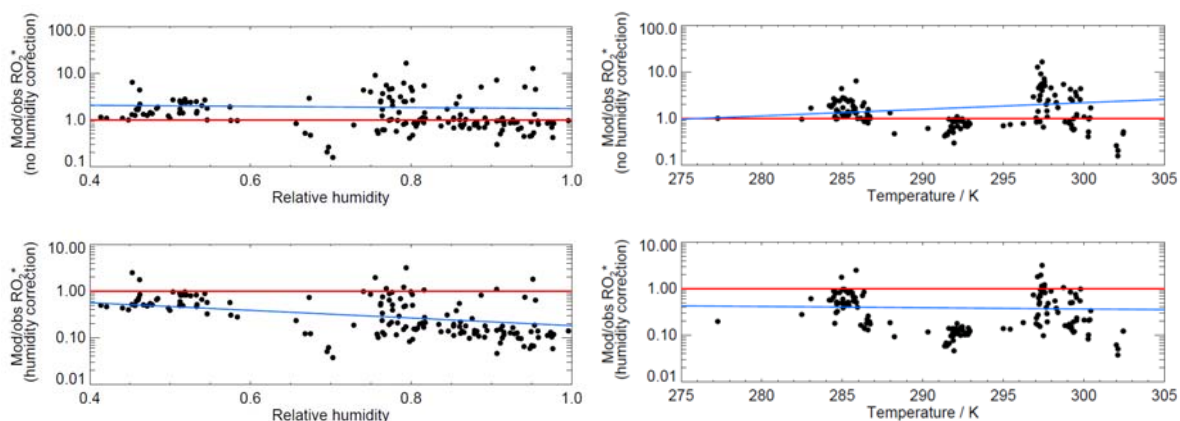

Fig. 4: DSMACC model to PERCA 4 measurement ratio as a function of a) relative humidity (as a fraction), and b) temperature (in Kelvin).

The model to measurement ratio as a function of temperature shows that the "humidity corrected" data consistently overestimates the model with no real trend. A slight increasing trend with temperature is observed in the "non humidity corrected" model to measurement ratio. This has no relationship to humidity and in fact can be explained the changing composition of the radical population with altitude (Brookes, 2009). Model to measurement agreement improves at higher altitude (lower temperature) where the radical population is primarily composed of HO_2 and CH_3O_2. At lower altitudes (higher temperature) a more complex population of organic peroxy radicals influenced by the surface emissions of isoprene is modelled and the increased model to measurement ratio reflects a reduced sensitivity of the measurement to these components of the radical population.

The text has been accordingly changed on page 8455.

II.5) Concerning condensation / icing on the sample inlet. Be more specific. Under which conditions do you expect these effects to be important? What was the temperature and humidity during the flight? It seems that the relative humidity was around 50% during the flight at lower altitude. Why would you expect the condensation to take place under these conditions? Can you present examples of measurements at high altitude (6km) at lower humidity when the icing was not important? This would support the hypothesis about the importance of the icing.

We expect condensation to occur when the air becomes saturated/supersaturated and icing to occur at when the temperature falls below freezing and significant amounts of condensation have occurred

preceding this. These conditions are often satisfied when profiling from low altitude within the monsoon layer to high altitude below freezing temperature. We cannot present examples of measurements at high altitude be sample flow control failed on every occasion we flew to high altitude.

II.6) Present any experimental, if available, or estimated influence of the condensation on the change of the humidity in the reactor.

We have no experimental data to quantify the change in humidity within our inlet compared to ambient levels. However as Fig. 6 (in the revised manuscript) indicates, our sample flow drops significantly as the temperature falls below freezing and simultaneously the water content changes from a mixed phase to condensed water (ice) only, indicated by the Nevzorov probe data from the BAe-146. We believe this is indicative of significant condensation and freezing (which then blocks the sample flow to the inlet) although we cannot currently quantify the level of condensation within the inlet in flight.

II.7) Finally, if the calibration of the instruments under conditions of the flight pressures and temperatures is available it should be applied to both instruments and than the data should be compared. Otherwise, one may conclude that the presented data are not reliable and that either such calibration measurements should be performed, or an in situ calibration should be used.

The pressure of the DUALER instrument is kept constant during the measurement and the corresponding laboratory calibrations at this pressure condition is applied for the analysis of the results. Performing calibrations at the expected atmospheric temperatures (between 20 and -50°C) is quite challenging due to the complexity of the required experimental set up. However, as stated above, the temperature of the DUALER inlet was above zero during the whole AMMA measurement campaign.

Laboratory calibrations can only partially simulate the ambient conditions during the airborne measurements. As stated by the referee it is of course desirable to perform in situ calibrations. The present manuscript is actually trying to attract the attention of the scientific community about the necessity of carrying out in situ calibrations and intercomparisons within airborne campaigns. This is in practice not the case due to time and financial constraints. The overall interpretation of measurements taken by different airborne platforms can be affected by significant bias and innaccuracies if the airborne platforms are not carefully intercalibrated and intercompared.

Concerning the PERCA 4, as discussed in the revisions to section 2.1.2, the NO_2 sensitivity is calibrated in situ, while in flight calibration of the CL was not possible. Instead, as stated, ground calibrations were carried out for the CL and modelling and experimental work was performed to assess the potential impact of changes in ambient conditions i.e. humidity (experimental and analytical assessment (Brookes, 2009)), temperature and pressure (model of the CL dependence (Brookes, 2009)). The purpose of the blind intercomparison is to use it to identify where there are systematic differences between measurement techniques and to identify how these may be addressed. The conclusions of the paper should include this discussion but the content of the paper should present the data as prepared "blind" without adjustment.

III) Comparison with the model.
As it stated many times by the authors, the main focus of the article is on "the analysis of the uncertainties of experimental data rather than on the comparison with model results". However, since such comparison is extensively presented in the article, it would be appropriate to present also some kind of a clear conclusion related to "the analysis of the uncertainties". On the basis of Fig.6, 7 and 9 the model does not only not reproduce the absolute concentrations and variability of the RO2 and HO2 radicals, but also fails to predict the profiles of other species (e.g. HCHO on Fig.9).

Taking into account the limitations of the modeling and the measurements detailed in the section 4.4., we actually believe that the modeling results agree reasonably with the measurements.

The text has been extended for clarification at the end of line 22 on page 8466:

"The major uncertainty in the model derives from the uncertainty in the measured photolysis rates. Model sensitivity to input parameters, is discussed in detail in Stone et al. (2010), and show that any overestimation of radical species in the model may be explained by the uncertainty in measured

photolysis rates. The model does, however, replicate the variability in observations, as shown in Figure 14 and evidenced by the r^2 correlation coefficient of 0.75 between the modelled and measured HO_2 concentrations."

IV) Conclusion
Conclusion a): see the comment II.6)

There is no experimental data to quantify the change in humidity within the PERCA 4 aircraft inlets compared to ambient levels. However, as Fig. 6 indicates the sample flow drops significantly as the temperature falls below freezing and simultaneously the water content changes from a mixed phase to condensed water (ice) only, indicated by the Nevzorov probe data from the BAe-146. The drop in sample flow is thought indicative of significant condensation and freezing, which may reduce the sampled humidity as a byproduct. The modelled reduction in the PERCA 4 chain length owing to the pressure and temperature dependencies of the chain chemistry reaction rate coefficients does explain a significant proportion of the systematic offset between the PERCA 4 and DUALER measurements. The demonstrated lack of a trend in the model to measurement ratio with relative humidity further supports the conclusion that under the conditions of the aircraft measurements the chain length is unperturbed by the ambient levels of humidity. The measurements otherwise show the same temporal variation and agree in magnitude within the instrumental uncertainties.

The text on page 8467 line 23 has been extended:

(a) *[RO_2^*-PERCA 4] and [RO_2^*-DUALER] agree within the instrumental errors when the correction for the expected humidity interference to the chain chemistry in the PERCA 4 instrument is not applied, while the [RO_2^*-PERCA 4] corrected data set remains unrealistically higher.* *The modelled reduction in the PERCA 4 chain length owing to the pressure and temperature dependencies of the chain chemistry reaction rate coefficients does explain a significant proportion of the systematic offset between the PERCA 4 and DUALER measurements. The demonstrated lack of a trend in the model to measurement ratio with relative humidity further supports the conclusion that under the conditions of the aircraft measurements the chain length is unperturbed by the ambient levels of humidity. The measurements otherwise show the same temporal variation and agree in magnitude within the instrumental uncertainties.* *This support the conclusion that it is inappropriate to use the humidity corrected data from the PERCA 4 instrument for the rest of the AMMA campaign.*

Some minor comments:
Section 4.3: Provide reference to "Brookes (2010)"

Incorrect reference – should refer to, Brookes (2009). It has been corrected on page 8464..

Fig.4: Provide a description for the data presented on Fig.4-3 by the blue line;

This figure caption was already extended as part of the modifications required by the editor before the publication in ACPD as:

"Figure 4: Variation of related trace gases during the AMMA radical intercomparison exercise: CO, O_3 NO_y, and HCHO as measured on board the D-Falcon, $(CH_3)_2CO$, CH_3COH, MEK, PAN and CH_3OH as measured on board the BAe_146. The $(CH_3)_2CO$ measured by PTR-MS (blue line) agree reasonably with the WAS samples (blue dots). The periods of the intercomparison are highlighted in the top figure in yellow."

In the revised manuscript is the figure 8.

Fig.9, "The model data are constrained as in Fig.6 and 7": The model constrains where different for the model 6 and 7. Also, the model used for the Fig.9 is not constrained by the HCHO data. Please correct.

The mentioned constraints of the model refer only to the photolysis rates. That is why the figure 9 can be compared in that respect to figure 6 and 7. The figure caption has been modified for clarification:

"Figure 9: [HCHO] measured on board the D-Falcon (dark blue circles) and modeled (blue) for the intercomparison exercise. The model data are constrained to $j(NO_2)$ and $j(O^1D)$ measured on board the BAe-146 (top) or to $j(NO_2)$ measured on board the D-Falcon scaled to the $j(NO_2)$-BAe values measured at 697 hPa (bottom) as in Figs. 6 and 7. The corresponding [HO_2] model data are also included for comparison."

This figure is in the actual revised version of the manuscript the figure 13.