Anonymous Referee #2
Received and published: 2 November 2009

General remark
This paper is submitted as a technical note. However, the present, very brief description of the instrumental setup and the experimental parameters make it very difficult to follow the discussion concerning the different pressure dependencies. Instead of using 3D-CAD screen shots of the apparatus I suggest to provide a schematic drawing of the instrumental setup used for the characterization experiments which shows the functional relationship between the different components. Adding labels like p_chamber,p_DUALER would help a lot to more easily understand the different figures in the paper.
A table with important experimental parameters would ideally complement such a figure for quick reference which is difficult at the moment as the parameters are "hidden"in the text.

The figures have been changed and a table with the summary of the instrumental parameters has been included according to the comments of the referee (see below)

Abstract
The authors claim to discuss the detection limit of the instrument. However, there is no discussion of the detection limit in the paper.

Section 4.2. has been extended to include a discussion of the detection limit as follows (the text added is underlined):

"4.2. Error analysis and <u>detection limit</u>

The calculation of the error associated with the RO_2^* mixing ratios must take into account the contribution of the following sources of uncertainty:

1. *NO_2 detector sensitivity. This is determined by the NO_2 calibrations with cylinders of known concentration (see Sect. 2.2) and the reproducibility is within 99% for laboratory measurements taken with the same filter and under the same pressure conditions. By using the procedure described in Sect.4.1, the relative accuracy of the NO_2 airborne measurements remains between 20% and 35%.*

2. *CL determination. The effective CL is determined at the laboratory for a particular measurement pressure with a 15% standard deviation. Potential in-flight losses of radicals before reaching the addition point in the reactor can only be estimated. These might be of significance in the presence of clouds or aerosols.*

<u>*The detection limit of the NO_2 detector is calculated as 3 times the standard deviation of 20s signal averages at each calibration point made at 200 mbar under laboratory conditions. This leads to a value of 0.13±0.05 ppb NO_2. As the eCL=45±7 at 200mbar, the RO_2^* detection limit is 3±2 pptv for 20s time resolution.*</u>

<u>*During AMMA.....*</u>*"*

p. 18273, Line 11ff
The quantitative and selective discrimination between HO_2 and RO_2 has been accomplished for a long time now by the Matrix Isolation Spin Resonance Technique (e.g. Mihelcic, D. et

al.: Numerical analysis of ESR spectra from atmospheric samples, J. Atmos. Chem., 11, 271–297, 1990).

We definitely agree with the referee. The text has been enhanced and the new literature reference (Mihelcic, D., Volz-Thomas, A, Pätz, et al.: Numerical analysis of ESR spectra from atmospheric samples, J. Atmos. Chem., 11, 271–297, 1990) included in the list of references:

"In recent years, both new detection techniques and substantial improvements in the characterisation of existing measurement techniques have been reported (Reiner et 10 al., 1997; Cantrell et al., 1996, 2003a, b; Green et al., 2003, 2005; Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003). The quantitative and selective discrimination between HO_2 and RO_2 was first accomplished by the Matrix Isolation Spin Resonance Technique (Mihelcic et al, 1990). The field deployment of MIESR is however limited by its high weight, delicate sampling procedure and long sampling time. Most recent developments aim at the speciation of peroxy radicals by using other techniques (Edwards et al., 2003; Fuchs et al., 2008)."

p. 18273, Line 29f
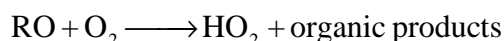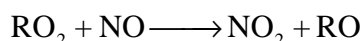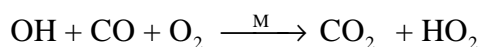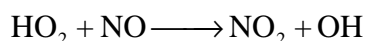**The capital L is missing in the extension of the DUALER abbreviation.**

This has been corrected. DUALER stands for **DU**al channel **A**irborne peroxy radical chemica**L** Amplifi**ER**)
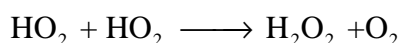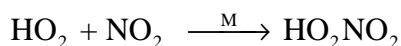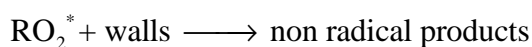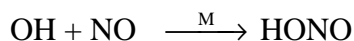
2.1 Description of the set up
I suggest to present the basic chemical reactions of the amplifier for those readers who are not familiar with the technique.

In Sect. 2 line 23 following text has been included according to the suggestion of the referee:

"….produced per peroxy radical and consequently the chemical amplification of the signal. The chain length is defined by the competition of the chain propagating reactions:

$$HO_2 + NO \longrightarrow NO_2 + OH$$

$$OH + CO + O_2 \xrightarrow{\ M\ } CO_2 + HO_2$$

$$RO_2 + NO \longrightarrow NO_2 + RO$$

$$RO + O_2 \longrightarrow HO_2 + \text{organic products}$$

and the chain terminating reactions, mainly being:

$$OH + NO \xrightarrow{\ M\ } HONO$$
$$RO_2^* + \text{walls} \longrightarrow \text{non radical products}$$

$$HO_2 + NO_2 \xrightarrow{\ M\ } HO_2NO_2$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

$$OH + HO_2 \longrightarrow H_2O + O_2$$
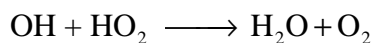
Under typical operating conditions, the radical-radical reactions play a negligible role in the termination of the radical amplification process.

A modulated signal is obtained by.....”

p. 18274, Line 25
... radicals decay quickly and only a few ppt of NO$_2$ are produced from the reaction of the sampled peroxy radicals with NO.

The sentence has been changed accordingly:

“In the absence of CO the peroxy radicals decay quickly and only a few ppt of NO$_2$ are produced from the reaction of the sampled peroxy radicals with NO.”

p. 18275, Line 12f
What is the inlet diameter of the reactors?

The inlet (orifice) diameter of the reactor is 10 mm. This information has been added to the existing sentence:

“The ambient air is mixed with NO and CO as soon as it reaches the reactors (21mm ID, 310mm L stainless steel cylinders, 10 mm inlet orifice) and this mixture….”

p. 18275, Line 25
Please be more specific: Data are acquired at a rate of ...Hz using a Data Translation interface ...

The text has been enhanced accordingly:

“Data are acquired with a DT 322 Multifunction Data Acquisition Board having an analog digital conversion rate of 200 kSA/s per channel, 30 Hz averages being saved. Homemade software is used to switch three way valves in the inlet system every 60 s alternating the modes of the reactors.”

p. 18276, Line 12
Please be more specific: gas mixture added to the converter: 3 ppmv NO in N2 and 7.4% v/v CO in synth. air? What were the flow rates? (N.B. these parameters should all go into a table)

The text has been slightly changed to prevent misunderstanding:

“…. onboard the DLR-Falcon, the flows of the NO and CO gases added were adjusted to reach 3 ppmv NO and 7.4% CO added to the ambient flow; the total sampling flow rate at each reactor being 0.5sLmin^{-1}. Table 1 summarises the operating flow conditions and concentrations during AMMA”

Gas	Flow rate (ml/min)	Reactor concentration
Sampling air	500	-
600 ppmv NO in N_2	2.5	3 ppmv
CO (99.97% purity)	37	7,4%
N_2 (99.999% purity))	37	≈ 75%
NO_2 1 ppmv in SA	10	20 ppbv

Table 1. Operating flow conditions at the DUALER reactor during AMMA

p. 18276, Line 21ff
Please be more specific (numbers) why during AMMA the proven dependency of the CL on RH is not important. What were the relative humidity in the ambient air and in the reactor?

Please see answer to referee1. On page 18276 line 23 the text has been modified for clarification:

"*The DUALER inlet is not heated during the AMMA flights but its inner part is connected to the cabin of the aircraft. As a consequence, the temperature of the reactors remains always higher than of the outside air. Therefore, the RH, being $RH = \left(P_{partial}^{H_2O} \middle/ P_{saturation}^{H_2O} \right)$, decreases in the reactors respect to the ambient as $T_{ambient} < T_{reactor}$ causes the increase in $P_{saturation}^{H_2O}$ and $P_{ambient} > P_{reactor}$ causes the decrease in the $P_{partial}^{H_2O}$ in the reactors (Kartal, 2009)*".

p. 18277, Line 12ff
Please provide figure of experimental setup (s. also General remarks)

The text has been extended on line 15 :

"*…. be evacuated down to 100 mbar. The experimental set up is depicted schematically in Fig.1 and main geometrical features are summarised in table 2*"

	DUALER pre-reactor nozzle	DUALER reactor	Pressure chamber
Orifice diameter	1m	10 mm	49,5 cm
Inner diameter	63mm	21mm	49,5 cm
Length	13mm	31mm	105 cm
volume	55cm^3	10,7cm^3	0.2 m^3

Table 2. Geometrical features of main components of the calibration set up

p. 18278, Line 23ff
What was the variability of the ambient pressure?

The ambient pressure, i.e., for these experiments the pressure of the chamber, once regulated presents a $\pm 0,15\,\%$ variability. This information has been included in the text:

"*Once the detector has stabilized at a particular pressure (i.e., ±0.15% variability), both signal and….*"

p. 18279, Line 4ff
better write: The extent of the chain reaction depends not only on the concentration of the reactants and the residence time in the reactor but also on the material ...

The text has been accordingly modified:

"*The extent of the chain reaction depends not only on the concentration of the reactants and the residence time in the reactor but also on the material and shape of the reactor, as it results from...*"

p. 18279, Line 10.
**Eq. (1) does not describe the pressure dependence of the CL.**

The text has been modified:

"*The pressure variation of CL for the reactors constituting the IUP-DUALER was determined experimentally using a HO_2 source in which the produced HO_2 is calculated according to Eq.(1)*"

p. 18279, Line 26f
What is the minimum retention time in the reactor to complete the chain reaction at 200mbar/1000mbar?

According to simulations made with a chemical box model including main involved reactions (described in Kartal, 2009), compared and in agreement with the simulations reported by Clemitshaw, et al. (A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements, J. Geophys. Res., 102, D21, 25405-25416, 1997), the minimum retention time required at 1000 mbar to complete the chain reaction is around 1,2 s. If the wall loss rate is assumed to be the same for 1000 and for 200 mbar, a minimum retention time of 1,8 s is calculated for 200 mbar (see figure below with the temporal CL evolution simulated at 200 and 1000 mbar (k_{wall}=1.5 s-1 for both pressure levels).
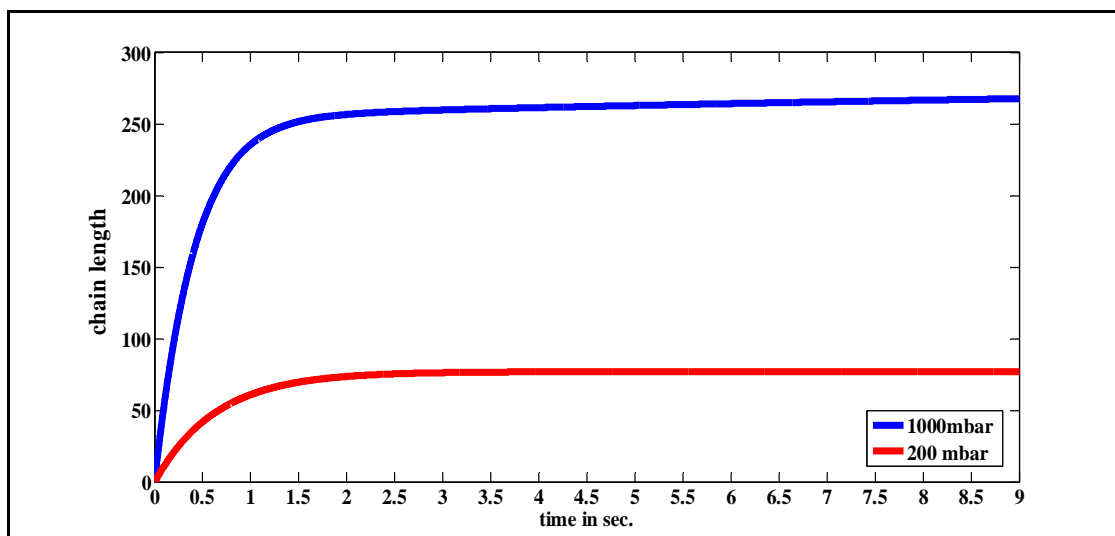
p. 18280, Line 6ff
I am confused by the different statements on how the pressure dependency of the wall loss is handled in the model: "The wall losses were constrained to the measurements at 1000 mbar and kept constant for the whole pressure range.",
"From the comparison with the experimental results (Fig. 6) the variation of the wall losses with pressure is estimated to be k_wall = 1.5-(P1/10*P2) ...". Do the authors mean k_wall = 1.5-(P1/(10*P2))? How does this value compare to the number listed in Tab. 1?

The text has been modified for clarification:

"A box model accounting for the main reactions involved (see Appendix A) was used to simulate the CL pressure dependency. The wall losses were constrained to the measurements at 1000 mbar leading to a $k_{wall}^{HO_2} = 1.5s^{-1}$, and kept constant for the whole pressure range. Generally the agreement is very reasonable but for P<400 mbar the simulations underestimate slightly the CL obtained experimentally. This indicates that the variations with the pressure are either underestimated for the propagating reactions or overestimated for the terminating reactions (see Sect. 2.2.). Provided that the increase of k_{CO+OH} with the pressure has been thoroughly studied (Sander et al, 2006), the discrepancies must be caused by the terminating reactions. The pressure variation of the experimental CL can be simulated by replacing k_{wall} with a total k_{loss} $k_{loss} = 1.5 - \left(\frac{P_1}{(10 * P_2)} \right)$, where P_1=1013.15 mbar, P_2 is the measurement pressure and k_{loss} is expressed in s^{-1}.

The number in table 1 is based on our experimental work. This information has been included in the caption of table 3 and the description in Appendix A has been modified:

"Table 3 Reactions used in the chemical box model. The rate coefficients are in units of $cm^3 molecule^{-1}s^{-1}$ except for the first order heterogeneous wall loss of HO_2 (based on the experimental data of this work) and the unimolecular decomposition of peroxynitric acid (HO_2NO_2) which are in s^{-1}."

p. 18281, Line 1
Reference should be to Fig. 7; P_sample should be P_chamber to be consistent with figure caption

The numbering of the figures has changed but the reference and the figure caption have been accordingly modified.

p. 18281, Line 1ff
The argument with the increasing gas velocity at increasing Delta_P is only true as long as P_DUALER > 0.5*P_chamber. A P_DUALER below this threshold will result in a supersonic gas expansion with no further increase in gas velocity.

This is true if referred to the orifice of the pressure nozzle. The velocity of the gas across the orifice will be constant for $P_{DUALER}/P_{chamber} < 0.5$.

However, we refer our interpretation to the whole pre-reactor nozzle of the DUALER, where our radicals can get lost before the amplification in the reactors takes place. For each pressure in the chamber the pressure regulator will set different mass flows to be sucked through the pre-reactor nozzle to assure that the DUALER pressure is kept constant, while the mass flow controllers in the DUALER itself make sure that the mass flow through the reactors are also kept constant. At higher $P_{chamber}$ the pressure regulation has to deal with a high volume flow in order to reach the 200 mbar set for the DUALER. When lowering $P_{chamber}$ the pressure difference between the chamber and the DUALER decreases gradually and as a result the volume flows through the pre-reactor nozzle are gradually smaller. High volume flows through the pre-reactor nozzle can enhance turbulences before amplification which favour radical wall losses. On the other hand, lower flows increase the residence time in the pre-reactor nozzle, and consequently the probability of radical wall losses.

The experimental eCL obtained (in Figure 7, now Figure 5) varies slightly over the range of pressures set in the pressure chamber. This variation, although it can be considered to be within the experimental variability indicated by the error bars, is very reproducible and therefore it is believed to be the result of a real physicochemical process. It is therefore hypothesised that over the pressure range probed there is a competition between the effect of varying turbulences and residence time of the radicals in the pre-nozzle chamber. At both pressure ends, i.e., at 200 and 1000 mbar, the predominant effect is different (longest residence time and highest turbulences respectively) but both effects lead to a maximum in radical losses and therefore to a minimum in the eCL. At about 500 mbar it seems to be a kind of compensation point which leads to the local maximum observed in the eCL.

The text has been only slightly modified for clarification:

"As expected, the eCL is lower than the CL determined for the single reactor without pre-reactor nozzle. When keeping the DUALER at a constant pressure the eCL remains fairly constant within reproducibility and there is no significant difference in the results obtained at 200 and 300 mbar. The light curvature observed in the results in Fig. 5 is though very reproducible. This is interpreted to be related to $\Delta P = P_{sample} - P_{DUALER}$. Due to the pressure regulation the air sample flows with higher velocity through the pre- reactor nozzle at higher ΔP, what minimises the radical residence time in the pre-reactor nozzle and therefore the likeness of wall losses. However, high velocities are associated with turbulences which might enhance wall losses in the pre-reactor nozzle. Low ΔP is linked to less turbulence but to longer radical retention times in the pre-reactor nozzle. At different ΔP the eCL is therefore the result of these competing mechanisms in the wall losses which may reach a compensation point at about 600 mbar."

p. 18281, Line 7ff

Even if the pressure in the pre-reactor nozzle is not regulated I would still expect a pressure drop across the 1mm nozzle. Do you have pressure measurements from the DUALER reactors at different chamber pressures?

This is true. If the pressure in the pre-rector nozzle is not regulated, it is to be expected a pressure drop across the pre-reactor nozzle. As the mass flow through the reactors is kept constant at each pressure, the volume flow increases as the pressure is decreased. This was not measured during the investigation. However, taking into account that the flow through the orifice is laminar, according to the Poiseuille formula the pressure drops expected vary between 0.2 and 6% for the worst case at 200 mbar (see plot).
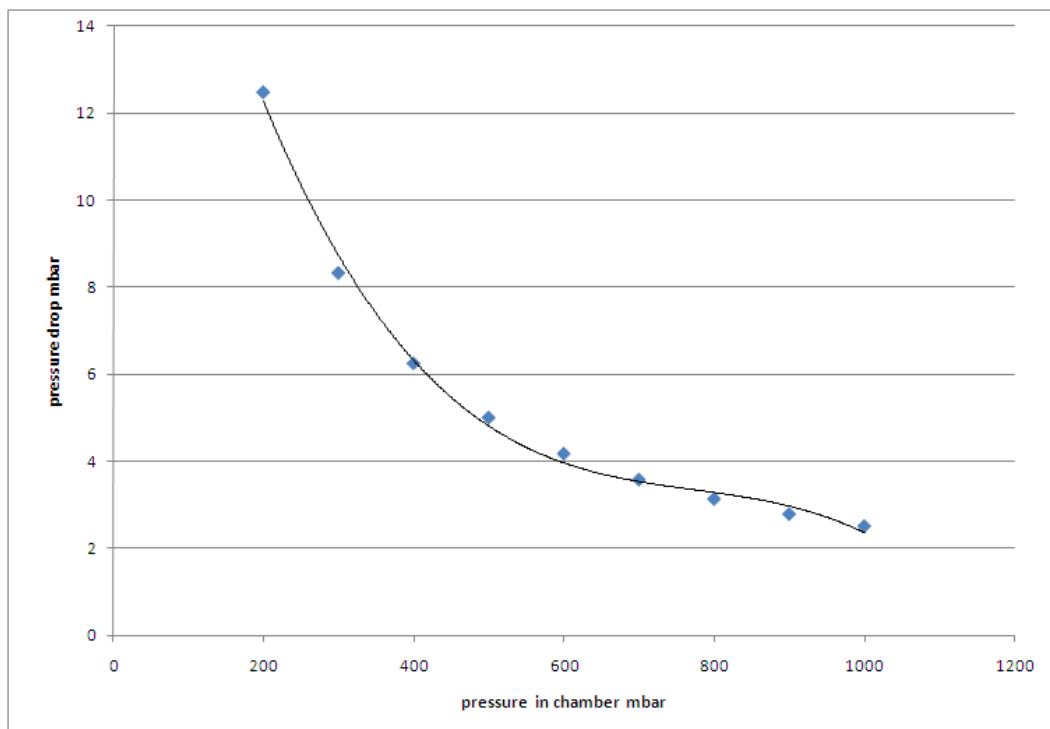
Following sentence has been modified in the text for clarification:

"This is confirmed by the results obtained when the DUALER pressure is not regulated, up to 500 mbar (Fig. 6). As the flow across the 1mm orifice of the pre-reactor nozzle is laminar, the pressure drop (P_d) for each chamber pressure can be calculated. P_d decreases from 12 mbar at 200 mbar to 2.5 mbar at 1000 mbar. Therefore, $\Delta P = P_{sample} - P_{DUALER} \cong 0$. "

p. 18281, Line 12ff
The authors discuss differences between the measurement series with and without pressure regulation which in view of the error bars are not significant. In fact, it is hard to see any difference at all between Fig. 7a and Fig 8 which is also evident from Fig. 9a.

This is discussed more in detail because it is one unexpected experimental result. As the pre-reactor nozzle is a radical trap, more radical losses were expected without pressure regulation as the retention time before amplification is higher. But the eCL obtained with and without pressure regulation are not significantly different. As stated in the text, this is interpreted to be the result of additional turbulences associated with the pressure regulation which favour wall losses of radicals in spite of diminishing the residence time in the pre-reactor nozzle.

p. 18283, Line 13ff
Velocity of gas sample through nozzle of the pre-reactor: see comment above

Please see answer above.

p. 18284, Section 4
What chain length was used for the evaluation of the AMMA data, eCL for pure HO2 or for a HO2/RO2 mixture?

The chain length obtained for pure HO_2 calibration gas has been used for the AMMA data analysis. As presented in section 3, the laboratory results indicate that this can lead to an

overestimation of the total RO_2^* which depends on the radical composition and likely varies between 8 and 15% for the HO_2/RO_2 ratios expected in the air masses sampled.

p. 18284, Line 17ff
Please provide some quantitative information on the reproducibility of the in-flight NO2 calibrations and the accompanying NO2 calibrations prior and past the measurement flights.

The calibration parameters obtained before the flight and after the flight are not representative of the response of the detectors during the flight as the luminol pump had to be turned off for a short time before the take off and after landing. According to our experience in laboratory experiments, interrupting the luminol flow affects the wetness of the filter and therefore the response of the detector. In addition, as the D-Falcon intended to characterise the MCS, most of the second half of each track was flown at altitudes corresponding with pressures lower than 270 mbar. Under these conditions the instrument detector cannot be kept at constant pressure and any calibration made afterwards cannot be representative of the previous performance of the detector during the flight. This is the case of the calibrations made after flight. In flight calibrations with cylinders were not possible.

The methodology to calculate the effective calibration parameters by comparison with the O_3 mixing ratios measured simultaneously as described in Sect. 4.1 was therefore developed and used as in-flight monitoring for the analysis while the calibrations performed before and after flights were used as additional information about the general performance of the instrument. The "a" parameters obtained from the O_3 in-flight validation within AMMA generally vary between 15 and 35 with a relative accuracy between 15-30%, in reasonable agreement with the "a" parameters obtained in hangar or in the laboratory, which vary between 10 and 30 with 3% accuracy.

The text has been modified for clarification:

"…. As a consequence, in-flight calibrations with this NO_2 cylinder were not possible."…… "The NO_2 calibrations of the detectors with external cylinders made before and after the flights were insufficient to monitor potential in-flight variations in the detectors sensitivity."

At the end of page 18288 before Sect. 4.2 the text has also been extended:

"Within AMMA the A_{Deti} parameters obtained from the O_3 in-flight validation generally varied between 15 and 35 with 15-30% relative accuracy, in reasonable agreement with the "a" parameters obtained in the laboratory, which varied between 10 and 30 with 3% accuracy".

p. 18285, Line 9f
Better write: "Provided that the signal measured in the background mode is essentially defined by ambient O3 converted to NO2 by its reaction with the added NO ..."

The text has been changed as

"Provided that the signal measured in the background mode is essentially defined by ambient O_3 converted to NO_2 by its reaction with the added NO and that the response of the luminol detector remains linear (i.e., $NO_2=aX+b$), the sensitivity of each detector for each single point k during a selected time interval can be calculated."

p. 18288, Line 6ff
It would be helpful to provide a figure which shows the application of this method to an actual set of data. I suggest to show for a particular flight level the ozone and NO2 traces, the measured background signal for one of the reactors, the derived a*(i) and b*(i) parameters (please provide number of data points used to calculate these parameters), and the A-value with standard deviation. Please provide numbers for all equations in this section.

The text has been accordingly modified and the figure 12 has been added. All the mathematical expressions have been numbered.

"*Figure 12 shows exemplary the application of the calculation procedure to the measurements at 330 mbar on the 13 August 2006. In Fig. 12a the [O_3] in ppbv is compared to the raw background signal of the luminol detectors in volts. Despite the offset of the signals, the temporal evolution agrees very reasonably as expected. According to the procedure described above, the effective calibration parameters are calculated (A_{Det1}=28.2±4.5; A_{Det2}=16.8±3.1; B_{Det1}=16.9±1.9; B_{Det2}=14.3±1.5) and used to obtain the mixing ratios depicted in Fig. 12b.*"

p. 18289, Section 4.2
In this section you should comment on error contributions due to unknown HO2/RO2 mixing ratios in view of the eCL used for the data evaluation. The relative accuracies which are quoted refer to the reproducibility of the NO2 calibration under flight conditions (as descr. in Sect. 4.1) and the eCL calibrations in the laboratory.
Please comment also on the accuracy of the RO2 concentration obtained from Eq. (1).

As stated in Section 3.3. the eCL was investigated for a 1:1 mixture of HO_2 and CH_3O_2 which are the peroxy radicals considered to be more likely in the upper troposphere. There is no information available about the relative distribution of peroxy radicals in the air masses sampled. Only during the radical intercomparison exercise (Andrés Hernández et al., ACP 2010) HO_2 and RO_2^* were shortly measured simultaneously and the results suggested a HO_2/RO_2 ratio close to 1:1. Complementary modeling results indicate that CH_3O_2 represents 90% of the alkyl peroxy radicals (Stone et al., ACP 2010). According to the results of the characterisation presented in figure 13 (now figure 11), this would lead to an overestimation of the RO_2^* of about 14%.

The text in section 4.2 has been extended:

"…

3. *Radical partitioning in the air sampled. The presence of peroxy radicals other than HO_2 lead to an overestimation of the RO_2^* which most likely remains between 8 and 14% for the expected HO_2/CH_3O_2 ratio as stated in Sect. 3.3. There is no information available about the relative distribution of peroxy radicals during AMMA except for the radical intercomparison exercise (Andrés Hernández et al., 2010) where the HO_2/RO_2 ratio remained close to 1:1. Complementary modeling results indicated that CH_3O_2 represents 90% of the alkyl peroxy radicals present (Stone et al., ACP 2010). "*
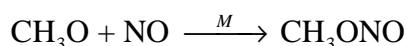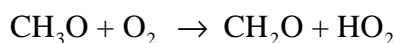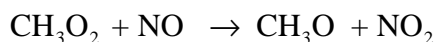
In addition, on page 18283, line 20 the text has been extended as follows:

"The wall losses of alkyl peroxy radicals are expected to be lower. A series of experiments were performed by using a methylperoxyl (CH_3O_2) / HO_2 radical source. This is achieved by adding methane (CH_4) instead of CO in the calibration gas:

$$H_2O + h\nu(\lambda = 184,9nm) \rightarrow H + OH$$

$$H + O_2 \xrightarrow{M} HO_2$$

$$OH + CH_4 + O_2 \xrightarrow{M} CH_3O_2 + H_2O$$
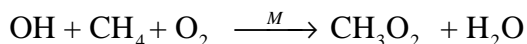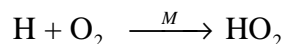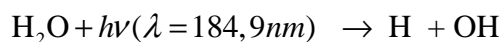
As CH_4 is added in excess to favour the chemical reaction over the OH wall losses, the source generates a 50% methylperoxyl (CH_3O_2) and 50% HO_2 radical mixture.

Once in the reactor, the HO_2 radicals lead the amplification cycle. The yield of HO_2 from CH_3O_2 for the experimental conditions is 0.85 [Clemitshaw et al., 1997] and results from the reactions:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$CH_3O + NO \xrightarrow{M} CH_3ONO$$

The eCL is therefore experimentally determined from the ΔNO_2 measured versus [HO_2] calculated by Eq. (1) for a 0.85 yield from CH_3O_2.

As expected, the eCL for the mixture of HO_2 and CH_3O_2 behaves similarly...."

Figures and Tables
General remark: Some attention should be paid to the layout of the diagrams. I suggest to use a common font for the axis title / legends in the different figures.
The Figs. 1-3 are not very instructive and partly hard to "read" (identification of indices in figures, e.g. where is index 4 in Fig. 3?). I suggest to exchange the 3D-CAD screen dumps against diagrams which show the functional relationship between the components (e.g. gas flow diagram).

Fig. 4.: Missing unit on Y axis. Please change legend for dark blue / red symbols (e.g. reactor 1 / 2)

Fig. 5.: Missing parentheses around unit in Y axis title

Fig. 6. Caption: ... as measured and modelled ... Gridlines would be helpful

Fig. 7-9: All these figures show plots of effective chain length against chamber pressure. Please use common X-axis titles, Legend text, and Y-axis range

Fig. 7.: Please add information on the HO2/RO2 mixture to the figure caption

Fig 15+16: It is very difficult to read the axis titles in yellow.

All the mentioned figures and figure captions have been changed according to the comments of the referee

Tab. 1. Caption: ... are in units of ... Missing entry: unimolecular decomposition of H2O2

The figure caption has been corrected. The entry was not missing but erroneously given as unimolecular decomposition of H_2O_2 though referring to the unimolecular decomposition of peroxynitric acid, PNA (HO_2NO_2).