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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxy radical observations over West Africa during the AMMA 2006 campaign: Photochemical activity in episodes of formation of convective systems on the basis of radical measurements" *by* M. D. Andrés-Hernández et al.

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Title. Part of the title does not really relate to the topic of the paper. That is the "...episodes of formation...". I suggest shortening and simplifying to "Peroxy radical observations over West Africa during AMMA 2006: Photochemical activity in the outflow of convective systems"

Thanks for the suggestion. The title has been changed to: "*Peroxy radical observations over West Africa during AMMA 2006: Photochemical activity in the outflow of*

convective systems"

Page 1588. It says that RO2 was measured by the DUALER instrument, but isn't it true that the instrument measures HO2 + RO2? If not, then the paper should describe how HO2 was removed from the signal. Also a reference to the Cantrell et al dual inlet instrument is appropriate here.

It is actually said that "RO_2^* was measured by using ...." and RO_2^* is defined on page 1588, line 7, as RO_2^*= HO_2+ RO_2.

As stated in the text, in Kartal et al. 2009, there is a more detailed description of the measured system, its characterisation and performance. Therefore other similar systems are cited there. However, it has now additional been introduced in this manuscript on page 1588 line 18, the sentence: "*Dual systems comprising two identical reactors and one or two detectors, have been developed in order to increase sensitivity and accuracy in the case of rapid changing background concentrations which can interfere in the radical determination [Cantrell et al, 1996 b, Green et al., 2003*]"

Somewhere (perhaps in the introduction), it would be helpful to describe the "expected" behavior of peroxy radicals in these outflow situations, since later in the paper comments are made that the behavior was "as expected" or "not as expected". I am talking about the functional behavior of peroxy radical concentrations versus NO concentration, clouds, and other variables.

On page 1587, the text from line 7 has been modified as follows (added sentences are in cursive):

"The mesoscale convective systems (MCS) enclosed into synoptic-scale African Easterly Waves during the West African Monsoon are considered to be the origin of about 40% of the Atlantic tropical cyclones and responsible for troposphere stratosphere exchange (Agustí-Panareda and Beljaars, 2008). Africa is therefore a suitable environment for investigating the photochemical activity in air masses impacted by MCS. Little

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is known about the chemical composition of these air masses during intense convective episodes. *The outflow boundary of a MCS provides focus for lifting, leading to effective transport of trace gases, aerosols and water vapor from the boundary layer into the free atmosphere. It is expected that the vertical transfer of oxygenated hydrocarbons and peroxides lead to enhanced O_3 formation as the peroxy radicals produced by UV photolysis react rapidly with NO which has also been vertically and horizontally transported, or produced by lightning. The total yield depends on UV radiation, potential losses of radicals (aerosols, clouds) and the vertical budget of radical precursors [Lelieveld and Crutzen, 1994, Cantrell et al., 2003a, 2003b]. In particular acetone can both be a source of peroxy and alkoxyradicals and affect the partitioning of odd nitrogen between NO, NO_2 and PAN [McKeen et al., 1997].*

HOx in the upper troposphere (6 to 12 km) cannot generally be sustained by the primary production of OH from the reaction of O^1D, produced by the photolysis of O_3 with H_2O and the subsequent reactions of OH with CO and O_3. Transported HOx precursors other than O_3 and H_2O seem to be the primary sources of hydrogen containing radicals in much of the upper troposphere (Wennberg et al.,1998). In the presence of enough NO from lightning, biomass burning, and aircraft emissions the resultant catalytic mechanism can be responsible for rapid and effective production of O_3 in the higher layers of the atmosphere and have a global impact (Jaeglé et al., 2001). Prather and Jacob (1997) suggested that given a 10 days overturning rate of the tropical upper troposphere, deep convection could cause a persistent chemical imbalance in HOy (defined as OH, HO_2 and their non-radical reservoirs, i.e., HO_y=OH+peroxy+$2H_2O_2$+$2CH_3OOH$+HNO_2+HNO_4). This has also been confirmed by the measurements of peroxides and CH3OOH of Cohan et al. (1999) in aged convective outflows in the tropical Pacific. Conversely, HO_x greater than the model predictions for high NO regimes (500–600 pptv) have been measured in biomass burning plumes encountered over the western Pacific equatorial region (Folkins et al., 1997)."

Page 1592. Plate 2 is referred to, but it should be Figure 2, I think.

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The idea was to express that there is a group of plots but as it is not consequently referred all over the text, and seems to lead to confusion, it has been changed to figure 2.

Page 1593, line 20. I didn't understand the phrase "...are not enough to make any conclusive interpretation." Perhaps there is a word or two missing here.

This refers to the HCHO measurement data. It stated: **"**The available DLR-Falcon measurements of HCHO at this pressure level (Fig. 2c) though presenting similarities with the NO and NOy pattern are not enough to make any conclusive interpretation**".**

And has been reworded as:

"HCHO was measured on the DLR-Falcon at this pressure level only up to 10:24 h (Fig. 2c). The general HCHO behaviour agrees roughly with the NO, NOy and RO_2^* patterns but it is not possible to definitely assign some of the short term RO_2^*variations to this potential HO_2 precursor, as HCHO is measured with lower time resolution"

Page 1594, line 16. Suggest "until" rather than "till". Suggest removing "down". Page 1594, line 17. Suggest removing "up".

The text has been accordingly changed.

Page 1594, line 19. Suggest a semi-colon before "if acetone".

The sentence "Similarly to the 15 August, as the NO/NO_2 ratio remains relatively high (around 7) most of the time, if acetone which has a lifetime of several days were simultaneously transported with NO, the production of radicals would be favoured" has been reworded:

"*Similarly to the 15 August, the potential transport of acetone simultaneous to NO would favour the production of radicals, as the NO/NO_2 ratio remains relatively high (around 7) most of the time*"

Page 1594, line 23. "Statistical error" is used, but don't you mean standard devi-

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ation of the averages?

Yes. The sentence: "The error bars depicted in Fig. 5b correspond to the statistical error of the 20 s averages**"** has been reworded for clarification:

"The error bars depicted in Fig. 5b correspond to the standard deviation of the 20 s averages from the 1s original data"

Page 1594, line 28. The role of clouds has been often discussed in the literature... Suggest adding one or two references here.

Following references have been added:

Seigneur, C., and Saxena, P.: The impact of cloud chemistry on photochemical oxidant formation, Water, Air, and Soil Pollution 24, 419-429, 1985.

Mauersberger, G., The influence of cloud chemistry on the budget of photo-oxidants, Transactions on Ecology and the Environment vol 6, WIT Press, ISSN 1743-3541, 1995.

Buxton, G.V., and Salmon G. A.: On the chemistry of inorganic free radicals in cloud water, Progress in Reaction Kinetics and Mechanism, 28, 257–297, 2003.

Shi, Q., Belair, S.D., Francisco, J.S., and Kais, S.: on the interactions between atmospheric radicals and cloud droplets: A molecular picture of the interface, PNAS, 100, 17, 9686–9690, 2003.

Page 1595, line 1. It says that there was no obvious correlation with formaldehyde, but one wouldn't expect a strong correlation if only a fraction of the HOx were formed from formaldehyde, correct?

This is correct. Thanks for the remark. The sentence has been extended:

"*No obvious correlation with HCHO is observed. However, as the DUALER measures the total sum of peroxyradicals, the absence of a strong correlation does not directly*

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ruled out that a fraction of HOx is formed from HCHO. Nor can be the presence of other sources of radicals from the oxidation of organic compounds excluded, as discussed above for isoprene."

(see answer to referee_2)

Page 1595, line 14. Sugest removing "down".

The text has been accordingly changed.

Page 1595, line 17. Does "outside the convection zone" refer to within the convective outflow?

The text has been changed to: "*The box model was initialised with..... representing different* RO_2^* */NO ratios within and outside the MSC convective outflow*"

Page 1597, line 24. Does the NOy really vary by 20 ppbv?

Yes. There is a minute with 1s mixing ratios peaking to NO 12 ppb, NOy 29ppb, CO 183 ppb, and the 1 min value of HCHO reaches 1.8 ppb.

Page 1598, line 13. Suggest rewording "..too different parameters and variables..."

The former sentence "It is normally difficult to acquire this detailed information, and even so, the comparison requires a normalisation which is complicated by the presence of too different parameters and variables" has been reworded to:

"*Generally, it is difficult to acquire this information at an adequate detail level, and even so, the normalisation of the different parameters and variables involved, previous to comparison is extremely complex*"

Page 1599, around line 8. Suggest adding a reference to the Ridley et al paper about convection as a source of UT NOx.

You probably refer to the publication:

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Jaeglé, L., Jacob, D. J., Wang, Y., Weinheimer, A. J., Ridley, B. A., Campos, T. L., Sachse, G. W., and Hagen, D. E.: Sources and chemistry of NOx in the upper troposphere over the United States, Geophys. Res. Lett., 25, 10, 1705-1708, 1997, doi: 10.1029/97GL03591

This reference has been included as suggested on page 1599. The text has been modified as follows (see also answer to referee_2):

"*Occasionally, simultaneous unexpected increases of NO and RO_2^* are observed, indicating the presence of a radical precursor, which is related to NO emissions. Jaeglé et al (1997b) interpreted the correlations between NOy and CO observed at 8-12 km altitude over the central US as indication of the primarily origin of NOx from convective transport of polluted boundary layer air. During the AMMA measurement campaign the NO_y and CO patterns often present similarities. However, the NO mixing ratios measured during the period by other aircrafts in the boundary layer are generally lower (Reeves et al.,2009), indicating that the NOx observed must be to a large fraction related to lightning episodes rather than being exclusively convective pumped to upper levels. Thunderstorms associated to MCS might also produce HOx and radical precursors as suggested by Zuo and Deng, [1999]. Lightning can cause decomposition of molecules like O_2, H_2O and N_2 and form reactive atoms and radicals which can recombine and lead to H_2O_2, O_3 and oxidized nitrogen species (Bhetanabhotla et al., 1985; Pinart et al., 1996; Coppens et al., 1998).*"

Page 1599, line 13. You mention significant O3 production rates (are these net rates, i.e. P-L) in the outflow. What are typical values in unaffected UT air masses?

The reactions considered for the calculation of O_3 production rates are included in the appendix A. All production rates discussed in this study are net production rates coming from the competition between formation and loss reactions, now including the chemical HNO3 formation (see answer below, page 1600) .

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The simulations on 4August 2006 (at 09:30 UT and 10:00 UT) are thought to be a comparison between O_3 production rates inside and outside a MSC outflow. As stated in the text, the humidity is used as tracer for the MSC outflow. At about 10:00 the aircraft was clearly outside the outflow zone and the corresponding measurements may be considered as representative for unaffected UT air masses. Our analysis indicates that within AMMA the net ozone production within the MSC outflow varies between 0.1 to 1.35 ppb / h, and in the potentially undisturbed UT air masses between 0.02 to 0.28 ppb / h.

Page 1599, line 27. "form" should be "from".

It has been corrected.

Page 1600. Should OH+NO2+M be in the mechanism?

Thanks for the remark. The HNO_3 formation (OH+NO_2+M) is a O_3 loss reaction and it has been now included in the box model according to Saunders et al., 2003. A sensitivity study has shown that the HNO_3 formation during the studied cases leads to a reduction in the ozone production of approximately 27$\pm$12%. However, as this reaction similarly affects all the examined conditions, the statements in the manuscript still remain consistent. All the ozone production rates have been accordingly recalculated. In addition, the chemistry in the box model has been extended in order to include the isoprene decomposition (see answer to referee_ 2).

Page 1602, line 1. Suggest "The presence of cumulus clouds are assumed with a ..."

This assumption actually concerns the cloud top height rather than the presence of the clouds itself. The sentence has been reworded as follows: *"The presence of cumulus clouds with a cloud top height well below the altitude of the aircraft has been assumed for this study."*

Figures. Suggest making all of the Pressure axes (such as Figure 2a) large at

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the bottom (1000 mB) and small at the top (like an altitude scale). Alternatively, actually change to altitude rather than pressure. On figures (such as 8) that have a variable plotted versus pressure or altitude, put the latter (P or z) on the y-axis. Also several plots have the x-axis labels at 0, but the y-axis minimum is less than zero (Figure). Suggest moving the axis labels to the minimum of the other axis (like Figure 9c).

The plots have been changed according to the suggestions of this referee.

It might be worthwhile to describe how "negative" concentrations come about and what

they mean in the analysis (e.g. Figure 12a and Figure 13).

The text on page 1597 line 14 has been extended as follows:

"*Figures 12 and 13 summarise the RO_2^* vertical profiles obtained on the 11, 13 and 15 August flights. RO_2^* up to 70 pptv with maximum mixing ratios between 400 and 700 mbar are observed. At a first glance the variability of the RO_2^* measurements seems to be large. Negative mixing ratios are occasionally calculated corresponding to signals measured close to the detection limit and presenting high variability around zero, as well as during very rapid changes in other trace species, clouds, humidity etc. In spite of the chemical meaningless of negative mixing ratios, these values are not removed as they are not caused by instrument failures and can provide useful information about radical variability and instrument response in a rapid changing environment. The analysis of data is however based on periods of stable conditions.*

A closer analysis of the data confirms that the general radical variability is mostly explained by the presence of clouds, acting as a variable sink of radicals, and by the variability of other controlling trace species like NOx, CO and VOC (Fig. 14). The former is the case for the measurements taken on the 11 August at 445 and 570 mbar and on the 13 August close to the surface, where the low and variable values of j_{NO2}(=0.006

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s^{-1}) are indicative of the presence of clouds. In addition, variations up to 20 ppbv O_3, 60 ppbv CO and 0.8 ppbv NO_x are detected within the same pressure level in some of the flights. On the 15 August the NO_y at 920 mbar vary up to 20 ppb. This indicates the existence of various vertical layers of different composition and photochemical activity."

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1585, 2009.