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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.

M. D. Andrés-Hernández et al.

Received and published: 20 April 2009

Specific comments

Abstract, Line 10. The phrase atmospheric layers should be changed to altitudes
This has been changed.

Introduction, Line 1 The first sentence in the text refers to organylperoxy radical.
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correct term is alkyl peroxy radical.

The term has been changed.

Introduction, Line 8. The phrase 30 degrees northern latitude should be changed to 30

degrees North to maintain consistency with the earlier part of the sentence.

This has been changed.

Experimental: Line 1-16 The authors describe the operation of the PERCA instrument used to make the measurements of HO₂ + RO₂ described in the paper, including operation of the instrument and uses terms and descriptions such as chain length, and amplification verses background modes. The reader is referred to another paper with respect to the instrument used in this study, but it would assist the casual reader of this paper to describe in more detail the operation of the PERCA instrument in order

to understand the experimental terms used in this section. The design, operation and function of the PERCA instrument is well documented in the literature and a more detailed list of references to this fact should also be included (e.g. Cantrell and Steadman 1982, Cantrell et al. 1996, Clemitshaw et al. 1997). Of particular importance is reference to the recent deployment of these instruments on aircraft (e.g. Green et al. 2003, 2006) as this is quite a new development in the measurement of radicals using the

PERCA technique.

We do agree with the referee on the importance of the quotation of previous work and developments. All these details and references above are already included in the manuscript cited [Kartal et al., 2009] which aims the detailed presentation of the measurement technique. Although the initial idea was to avoid redundancy, as result of this comment, following text has been added on line 3 of the experimental:

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“PERCA is one of the most frequently used measurement technique for the total sum of peroxy radicals. The method has been gradually characterised and improved and there is abundant literature about its deployment for ground based measurements in diverse polluted and remote areas (e.g. Cantrell et al., 1996a; Monks et al., 1996; Carslaw et al., 1999; Burkert et al., 2001a-b, 2003; Andrés Hernández et al., 2001; Volz-Thomas et al., 2003; Zanis et al., 2003, Fleming et al., 2006a-b). In most of the cases, the measurement system consists of a single reactor and detector. However, for remote areas and airborne measurements, 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]. Briefly, the DUALER...”

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Experimental Section 2.1, Line 18. The authors claim that the NO₂ standard used to calibrate the PERCA instrument was not stable due to high temperatures and humidity causing wall losses. Did the authors prove in lab based experiments that such temperature and humidity changes cause the fluctuations as they saw during the aircraft campaign? Also, what are the drawbacks and likely propagation of errors in using the mathematical method based approach they describe? This section need to be explained in considerably more detail.

As in the previous comment, the points raised by the referee are discussed in detail in the manuscript cited [Kartal et al., 2009] which focuses on the data and error analysis. We do believe that a very detailed explanation at this point would be to the detriment of the focus of the present paper. However, the last sentence at the end of 2.1 has been extended as follows:

“To overcome these issues and to monitor potential changes in the sensitivity of the detector during the flight, a mathematical method based on the O₃ concentrations simultaneously measured on the DLR-Falcon has been developed. Provided that the NO₂ background is essentially defined by the ambient O₃ mixing ratios 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 from two consecutive O₃ measurements at the time k and $k+1$. In order to rule out errors related to a malfunction of the O₃ instrument or to sudden variations of background ambient gases other than O₃ but providing NO₂ to the DUALER, a careful analysis of the involved parameters is made in order to determine the error for any particular selected time interval. The mathematical procedure and propagation of errors is described more in detail in Kartal et al. (2009).”

Concerning the fluctuations of the NO₂ cylinder, it is not trivial to simulate in the lab the environmental conditions with high T and humidity gradients *suffered* during the measurement campaign in Africa. Our interpretation of results bases on our observations in situ and on the information obtained in our discussions with the manufacturer. The

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high humidity conditions and the temperature gradients can promote the formation of HNO_3 on any surface in contact with the gas which may have traces of water. This can affect significantly the results specially if dealing with cylinders with low concentrations of NO_2 , as was the case (1ppm NO_2 in synthetic air).

Experimental Section 2.1, Line 19. The phrase possibly caused that does not make sense and should be reworded.

The sentence has been changed: *“This is attributed to the high temperatures and humidity reached in the aircraft prior to the flight which possibly led to changes in the wall losses at the pressure regulator and gas tubing in spite of long flushing of the gas lines “*

Experimental Section 2.3, Line 10 The authors describe that the trajectory densities were normalized to 1. I do not understand why this was necessary. This section should be clarified.

The trajectory density maps are normalized to one to become independent from the actual number of trajectories being discussed for the specific case. The maximum trajectory density is to be expected in the vicinity of the release area. The release points of the regarded trajectories were equally distributed within a spatial and temporal (=4-dimensional) volume centered at the location of the air craft observation. This volume has an extension of $0.6^\circ \times 0.6^\circ$ degrees (horizontally) x 1000m (vertically) x 1 h (time).

The text has been extended as follows:

“For the analysis of AMMA data the trajectory density bases on a grid of $0.25^\circ \times 0.25^\circ \times 100$ m. Subsequently the trajectory densities are normalised to 1 to derive a quantity which is independent from the actual number of trajectories discussed for the specific case study. This step is performed for each 2-dimensional projection independently. A similar approach is reported by Eneroth et al.(2003).

Eneroth, K., E. Kjellstrom, K. Holmen, A trajectory climatology for Svalbard; investigat-

ing how

atmospheric flow patterns influence observed tracer concentrations , Physics and Chemistry of the Earth, 28, p. 1191–1203, 2003.

Results, Line 2. The text refers to the uncertainty in the HO₂+ RO₂ measurement. I could find no overall assessment of errors in the data presented here, only later on line 77 of the results section. Presumable the associated error mentioned on line 77 was the same as that described here and was determined and described in a secondary paper. The percentage error of 45% should be quoted with references to direct the reader to how this error was determined.

As mentioned above, the errors in the measurement data are analysed in detail on the manuscript Kartal et al, 2009. However, following text has been included for clarification at the end of section 2.1:

“The error associated to the measurement of RO₂^{} is defined by the uncertainties in the determination of the NO₂ detector sensitivity and of the chain length. Laboratory NO₂ calibrations with cylinders of known concentration have generally a reproducibility within 99%. By using the procedure described in Kartal et al. (2009), based on O₃ measurements, the relative accuracy of the NO₂ airborne measurements remains between 20% and 35%. Concerning the CL, its laboratory determination at a particular pressure is subject to a 15% standard deviation.*

The propagation of the errors above leads to a total error between 25 and 45% for the RO₂^{} measurements performed during AMMA, depending on the flight conditions and the stability of the measurement signals for any particular measurement interval. Potential in-flight losses of radicals in the reactor before reaching the addition points caused by the presence of clouds or aerosols can only be estimated.”*

Results, Line 12. The authors used the data from CO, HCHO and CO₂ to determine the likely VOC concentration in the airmasses sampled. Although this

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procedure is fairly standard in the community, the casual reader would benefit from a more detailed description of why this is possible with suitable references.

The approach used in the present work is actually only qualitative. CO, HCHO and CO₂ have only been used as tracers for the potential presence of other VOCs but without any kind of quantification.

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Results, Line 23. The text describes peroxy radical reactions. These should be explained clearly with the use of equations, or reference to relevant reactions included in Appendix A.

On line 23 it has been included: "(see CO and CH₄ oxidation in Appendix A)"

Results, Line 28. The phrase in the presence of radicals is obsolete.

The sentence "*This leads to an O₃ production in the presence of radicals*" might be misleading and has been modified as: "*The in situ production of radicals and subsequent reaction with the present NO leads to O₃ production*"

Results, Line 30 Data suggest an ozone production of 1.7 ppb per hour. This number should be put in context with literature data for similar studies.

The sentence on line 27 has been completed as follows: "*Box model calculations. is responsible for an O₃ production of approximately 1 ppb hour⁻¹. This value is in reasonable agreement with the 4-8 ppb day⁻¹ production rates calculated by other modeling studies in MCS outflows during AMMA assuming different VOC and dilution patterns (Schlager et al, 2009). Cooper et al., (2006) reported large upper tropospheric O₃ enhancements up to 24 ppbv above midlatitude North America during the summer, and estimated in 80% the contribution of the O₃ in situ production from lightning and in 20% this of O₃ transport from the surface or in situ production from other sources of NO_x. Lower O₃ production rates have been observed in the upper troposphere in other seasons. Jaeglé et al. (1999) calculated O₃ production rates up to 2 ppb day⁻¹ for the measurements taken at 8-12 km during the SONEX campaign over the North Atlantic in winter. Miyazaki et al., (2003) estimated 0.5–4.4 ppbv day⁻¹ net O₃ production rates in the upper troposphere over East Asia in springtime*".

Results, Section 3.1. As stated previously, equations showing or referencing the radical

chemistry would benefit the casual reader.

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The text has been extended (see next comment below) in order to address this point.

Results, Section 3.1. Line 11-16 The data presented here are most interesting. The authors speculate on the existence of an unknown radical precursor, simultaneously emitted with NO. Clearly this is the only conclusion based on the data, yet the authors make no attempt to suggest a possible identity of this precursor. Did the authors attempt any scenario modelling i.e. suggest a possible identity for this radical precursor, and the concentrations necessary to cause the observed concentrations of RO₂? Also, since the concentration of ozone is constant at the time where the concentration of RO₂ and NO both increase, presumably the rate of production of RO₂ must be larger its rate of loss through its reaction with NO, and subsequent photolysis of the resultant NO₂ into ozone. This fast photochemistry should be discussed in more detail.

The present manuscript focuses mainly on the presentation and first interpretation of the experimental results. It attempts the modeling of a simplified chemistry just to give a first estimation of the photochemical activity associated to the measured air. Given the heterogeneity of the air masses sampled, the detailed modeling of the local chemistry all over the campaign is out of the scope of this paper. We do agree with the referee regarding the interest of the potential precursors of radicals, and detailed modeling studies are planned for further investigation of case studies. In order to address the questions of the referee some additional model runs have been performed and the following text has been included on results, section 3.1. line 38 :

“Bechera et al., (2009) presented recently vertical isoprene profiles measured during the AMMA campaign on board the French Falcon. Their results evidence the impact of the deep convection in the composition of short lived VOC in the upper troposphere. Isoprene mixing ratios up to 0.3 ppbv were detected between 8-11 km altitudes, in spite of its biogenic origin and less than 2 h life time. In order to estimate the impact of isoprene as in situ source of peroxy radicals, the reaction mechanism for isoprene decomposition suggested by Meyer-Arnek et al.(2005) was included in the box model

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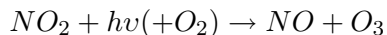
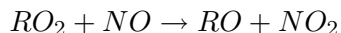
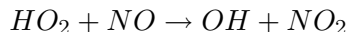
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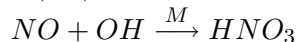
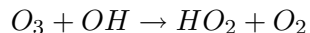
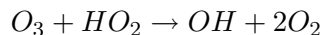


presented in Appendix A. It bases on the simplification of the chemistry on the Master Chemical Mechanism version 3.1 (Saunders et al., 2003) focusing on the species being either involved in the NO_x-HO_x-cycle or in the isoprene decay.

Once the radicals are produced, the net O₃ production comes from the competition between formation:



and O₃ loss reactions:



Different model runs were performed for different NO_x and isoprene mixing ratios representative of the observations. According to these, the injection of 0.1 to 0.2 ppbv isoprene in upper tropospheric layers can be directly responsible for an increase up to 6-7 times in the amount of peroxy radicals. In the presence of NO_x mixing ratios varying between 0.2 and 0.6 ppb the so formed peroxy radicals lead to a 20-25% increase in the net O₃ production. These results are in reasonable agreement with the measurements.”

Conclusions Line 14. The authors speculate that thunderstorms could produce HO_x or radical precursors from VOC decomposition. How would this be possible? Once again, equations and or reference would help clarify the statement.

Line 14 has been modified as follows: “Thunderstorms associated to MCS might also produce HO_x and radical precursors as suggested by Zuo and Deng, [1999]. Lightning can cause decomposition of molecules like O₂, H₂O and N₂ and form reactive atoms and radicals which can recombine and lead to H₂O₂, O₃ and oxidized nitrogen species

(Bhetanabhotla et al., 1985; Pinart et al., 1996; Coppens et al., 1998)."

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

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