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**Peroxy radical
partitioning during
AMMA**

M. D. Andrés-Hernández
et al.

Peroxy radical partitioning during the AMMA radical intercomparison exercise

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Abstract

Peroxy radicals were measured onboard two scientific aircrafts during the AMMA (African Monsoon Multidisciplinary Analysis) campaign in summer 2006. This paper reports results from the flight on 16 August 2006 during which measurements of HO₂ by laser induced fluorescence spectroscopy at low pressure (LIF-FAGE) and total peroxy radicals (RO₂^{*}=HO₂ + ΣRO₂, R= organic chain) by two similar instruments based on the peroxy radical chemical amplification (PerCA) technique were subject of a blind intercomparison. The German DLR-Falcon and the British FAAM-BAe-146 flew wing tip to wing tip for about 30 min making concurrent measurements on 2 horizontal level runs at 697 and 485 hPa over the same geographical area in Burkina Faso. A full set of supporting measurements comprising photolysis frequencies, and relevant trace gases like CO, NO, NO₂, NO_y, O₃ and a wider range of VOCs were collected simultaneously.

Results are discussed on the basis of the characteristics and limitations of the different instruments used. Generally, no data bias are identified and the RO₂^{*} data available agree quite reasonably within the instrumental errors. The [RO₂^{*}]/[HO₂] ratios, which vary between 1:1 and 3:1, as well as the peroxy radical variability, concur with variations in photolysis rates and in other potential radical precursors. Model results provide additional information about dominant radical formation and loss processes.

1 Introduction

Hydroperoxy- (HO₂) and alkyl peroxy (RO₂; R= organic chain) radicals are involved in many of the oxidation mechanisms taking place in the troposphere. They are short lived species originating from the oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) (Monks, 2005). Their reactions are closely coupled with those of the most important atmospheric oxidative agent, the hydroxyl radical OH, and the formation mechanisms of chemically or toxicologically important pollutants like ozone (O₃), peroxy acetyl nitrate (PAN), aldehydes, acids, etc. Knowledge of the atmospheric

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radical content and radical distribution provides essential information about the oxidative state of an air mass. In spite of their importance in the chemical processing of the troposphere, only a very limited number of airborne peroxy radical measurements are available (Brune et al., 1998; Jaeglé et al., 2001; Hanke et al., 2002; Cantrell et al., 2003a, b; Martinez et al., 2008). In particular, there are no previous measurements in or over Africa.

Within the European Project AMMA (African Monsoon Multidisciplinary Analysis) the fast photochemical processing during the West African Monsoon (WAM) period was investigated. Overall the AMMA project aims to improve the knowledge about the WAM variability and the impact on the local and global atmospheric composition. One of the main scientific objectives was to investigate the development of Mesoscale Convective Systems (MCS), including their impact on the transport of trace gases. For this, 5 different instrumented aircrafts were deployed within AMMA covering the measurement of trace gases over a broad vertical and horizontal area (Reeves et al., 2010). The importance of convection in determining the abundance of radical precursors in the Upper Troposphere (UT) has recently been confirmed experimentally within AMMA by Bechara et al. (2009), who measured enhancement of isoprene and other VOCs up to 10 km altitude within MCS episodes. Some of the products of isoprene oxidation have lifetimes of several hours, and it is possible that such compounds, as well as brominated and iodinated hydrocarbons, are locally transported to the UT by convective activity. Peroxy radical observations made within AMMA (Andrés-Hernández et al., 2009) are indicative of enhanced in situ production of peroxy radicals in the upper troposphere during convective episodes, linking the boundary layer, free troposphere and UT/LS chemistry.

The general interpretation of the impact of radical chemistry relies consequently on the data quality control designed to prevent any misinterpretation of results derived from offsets or other kind of instrumental artefacts. The intercalibration of similar instruments is a crucial part of the data analysis and interpretation, and the results obtained can be used to provide an estimate of the uncertainty associated with the airborne

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measurement of radicals. As reported by Reeves et al. (2010) wing tip to wing tip comparison flights along straight and level runs at various altitudes were performed during AMMA. The present work focuses on the comparison and evaluation of peroxy radical measurements.

2 Experimental description

Three instruments for the measurement of peroxy radicals participated in the inter-comparison exercise which took place on the 16 August 2006. Figure 1 depicts the corresponding flight track over the MSG (Meteosat Second Generation) satellite image at 15:00 h with IR brightness temperature. These images were usually used to locate the MCS during AMMA. The German DLR-Falcon (hereafter referred to as D-Falcon) and the British FAAM-BAe-146 (hereafter referred to as BAe-146) flew wing tip to wing tip for approximately 30 min, first in a straight and level westward run at 697 hPa followed by a straight and level eastward run at 485 hPa over the same geographical area in Burkina Faso. More details of the intercomparison including the results for measurements of CO, O₃, CO₂, HCHO and NO_y are given in Reeves et al. (2010). Results of the initial CO comparison led to a comparison of standards which showed that the data for the D-Falcon and BAe-146 should be corrected by a factor of 0.997 and 1.069, respectively.

Table 1 summarises the instrumentation in both aircrafts used for the present data analysis. A more detailed description of individual instruments is included in the following sections

2.1 Peroxy Radical Chemical Amplification

The Peroxy Radical Chemical Amplification technique (PeRCA) utilises the amplified conversion of the peroxy radicals entering the reactor into NO₂ in a chain reaction

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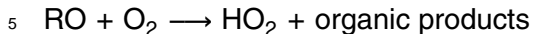
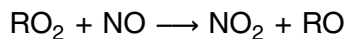
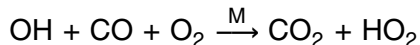
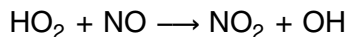
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involving NO and CO, namely:



By switching the addition of the reagent CO with an identical flow of N₂ between the front and back of the reactor the chain chemistry is modulated between *chain amplification mode* (i.e., NO₂ from the conversion of peroxy radicals plus other background trace gases producing NO₂ in their reaction with NO like O₃, plus NO₂ itself) and *background measurement mode* (i.e., NO₂ comprising that in outside air plus other background trace gases producing NO₂ in their reaction with NO). NO is added continuously at the front of the reactor, such that in *amplification mode* NO and CO are added together and N₂ is added at the back, while in *background mode* NO and N₂ are added together with CO added at the back. This methodology maintains the overall properties of the reagent mixture in the sample airflow downstream of the reactor and reduces pressure pulsing on switching measurement modes.

The chemiluminescence of the reaction of NO₂ with luminol (3-aminophthalhydrazide: C₈H₇N₃O₂) is used to measure the NO₂. The amount of peroxy radicals is calculated from the difference between the signals in both modes, ΔNO₂, and the knowledge of the amplification factor or chain length (CL) and radical loss at the inlet. PerCA measures the total sum of RO, OH, HO₂ and RO₂ radicals. As Σ[RO₂] ≫ Σ[RO] and [HO₂] ≫ [OH] in the troposphere, the measured signal is a good approximation of the total sum of peroxy radicals (RO₂* = HO₂ + ΣRO₂).

The CL depends on humidity (Mihele and Hastie, 1998; Mihele et al., 1999; Salisbury et al., 2002; Reichert et al., 2003), residence time in and shape and material of the reactor, and on the ratio of the gases added for the chemical conversion, i.e., [NO]/[CO].

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Instruments based on PeRCA have been developed for the airborne measurement of peroxy radicals (Green et al., 2003). In order to increase sensitivity and accuracy, dual systems comprising two identical reactors, which concurrently measure in the same or alternate modes, are coupled with one or two detectors (Cantrell et al., 1996; Green et al., 2006). Interferences related to short term variations of concentrations during the airborne sampling cycle are thereby minimized.

2.1.1 DUALER (*DU*al channel *Air*borne peroxy radical *chemical amplifier*)

As indicated in Table 1, the Institute of Environmental Physics of the University of Bremen (IUP-UB) participated in the wet monsoon measurement campaign of AMMA in August 2006 with the measurement of the total sum of peroxy radicals, RO₂^{*}, onboard of the German D-Falcon using a DUALER.

The airborne DUALER deployed on the D-Falcon has been developed by IUP-UB from the first calibrated PeRCA (Hastie et al., 1990) which has been gradually improved and implemented in several campaigns and comparison exercises for ground based measurements (Zenker et al., 1998; Andrés Hernández et al., 2001; Burkert et al., 2001a, b, 2003). This instrument bases on the concept described in Sect. 2.2. for aircraft measurements. The IUP-UB DUALER utilises a common inlet, and comprises a double reactor (21 mm ID, 310 mm L stainless steel cylinders, with a 10 mm inlet orifice) sampling from a common pre-reactor nozzle and connected to two identical luminol detectors. Three way valves in the inlet system are switched every 60 s and alternate the modes of the reactors. The DUALER is kept at a below ambient, constant fixed pressure during the measurement. The CL decreases with the pressure and the sensitivity of the instrument reaches a maximum for an operating pressure around 500 mbar. During the intercomparison exercise the DUALER was kept at 300 mbar. The characterisation, calibration procedures and performance during the measurement campaign are described in detail elsewhere (Kartal et al., 2010).

The known dependency of the CL on the relative humidity (RH) of the air sampled (Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003) has a negligible

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effect under the AMMA measurement conditions. 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 $RH = \left(P_{\text{partial}}^{\text{H}_2\text{O}} / P_{\text{saturation}}^{\text{H}_2\text{O}} \right)$,

reactors respect to the ambient as $T_{\text{ambient}} < T_{\text{reactor}}$ causes the increase in $P_{\text{saturation}}^{\text{H}_2\text{O}}$, and $P_{\text{ambient}} > P_{\text{reactor}}$ causes the decrease in the $P_{\text{partial}}^{\text{H}_2\text{O}}$ in the reactors (Kartal, 2009). The in flight detection limit and accuracy of the instrument depend on the stability of the luminol flow, the variability of the air mass composition sampled and the operating pressure. For most of the AMMA airborne measurements the relative accuracy was between 25 and 45% and the RO_2^* detection limit varied between 2 and 5 pptv for a 20 s time resolution (Kartal et al., 2009).

2.1.2 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, and was first described by Green et al. (2006). The characterisation, calibration procedures and performance during the measurement campaign are described in Brookes (2009).

PERCA 4 uses two equivalent channels each comprising a low-volume pyrex inlet coupled to a modified LMA-3 detector channel. The chain chemistry in each inlet is modulated between chain amplification mode and background measurement mode by switching the addition of the reagent CO with an identical flow of N_2 between the front and back of the inlet (typically every 60 s) while NO is added continuously at the front of the inlet. The channels are run out of phase to provide simultaneous measurements of chain amplified and background NO_2 , allowing the radical amplified signal to be determined by background subtraction.

The PERCA 4 inlets sample the airflow at ambient air pressure perpendicular to the aircraft direction of flight. The inlets can be heated to reduce the impact of humidity on the chain length, 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 are expected to remain at ambient levels on sampling and impact on the chain length. Temperature and pressure modify the chain length through the temperature and pressure dependencies of the PerCA chain chemistry. A systematic reduction in the chain length with altitude (of the order 20% at 700 mbar) has been modelled (Brookes, 2009) and the trend has been verified by comparison to the in flight chain lengths reported by Green et al. (2003). This may contribute to any 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 for altitude.

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 [RO₂^{*}] dataset (Brookes, 2009). On application of the correction to the AMMA dataset the concentrations typically scaled by a factor of 3–5 and lead to spuriously high values (Brookes, 2009). By comparison of the uncorrected PERCA 4 [RO₂^{*}] 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 and thus it may be inappropriate to apply the humidity correction to this dataset and therefore the intercomparison was made using the uncorrected data.

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

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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). Although the condensation of water vapour prior to the reaction zone may reduce the impact of humidity on the chain length, significant sampling losses of HO₂ are expected (Brookes, 2009) as reported by Green et al. (2003). Systematic differences in the RO₂^{*} measurements may then be attributed to the relative sensitivity of the respective PerCA instruments to inorganic and organic peroxy radicals.

The PERCA 4 inlet chain lengths were calibrated following the AMMA campaign in reference to known concentrations of the methyl peroxy radical, for details see e.g. Green et al. (2003). The accuracy of the derived RO₂^{*} concentration will depend on the relative proportion of the radical population made up by the methyl peroxy radical and radicals with a similar effective chain length. The estimated accuracy of the PERCA 4 measurements is of the order 40%, not accounting for uncertainty introduced by variation in the CL by altitude and systematic differences introduced by the weighting of the response by the CL with respect to the methyl peroxy radical.

2.2 Fluorescence Assay by Gas Expansion (FAGE)

Fluorescence Assay by Gas Expansion (FAGE) is a low pressure laser-induced fluorescence technique used for the detection of OH and HO₂. The instrument and associated calibrations are described in detail in Commane et al. (2010) and only a brief overview will be presented here. During the intercomparison flight described here, only HO₂ was observed. OH was not observed due to technical problems during the period of the campaign.

In this instrument HO₂ is titrated to OH by the addition of pure NO (99.999%). Air was sampled from a side-mounted inlet through a 0.75 mm pinhole into the fluorescence cell. A Nd:YAG pumped Ti:Sapphire laser is used to generate light at $\lambda \approx 308$ nm in order

to excite the Q1(2) transition of the OH molecule. The exact excitation wavelength is determined using a reference cell. The subsequent fluorescence of the OH molecule is also detected at $\lambda \approx 308$ nm. Maintaining the fluorescence cell at low pressure (1.5–2.5 Torr) allows for temporal gating of the fluorescence detection. The sensitivity of the instrument to HO₂ was determined by calibration before and after the campaign. In these calibrations, a known concentration of HO₂ is produced by the photolysis of water vapour (at $\lambda = 184.9$ nm) in a turbulent flow of air. The HO₂ data was collected at 1 Hz and averaged to 60 s for comparison here. The mean limit of detection of the instrument for the data discussed here is 0.31 pptv (60 s integration time).

2.3 Further instrumentation

A complete description of the aircraft instrumentation during AMMA can be found elsewhere (Reeves et al., 2010). For the data analysis of the present work, O₃, CO₂, CO, HCHO and reactive organic compounds measured on board the D-Falcon by using respectively UV absorption (Schlager et al., 1997), IR absorption (Schulte et al., 1997), UV fluorescence (Gerbig et al., 1996), a fluorometric technique (Hantzsch reaction), and two O₃/NO-chemiluminescence detectors and a gold converter for reduction of higher oxidized NO_y compounds to NO (Schlager et al., 1997; Ziereis et al., 2000) were used. The NO_x was also measured by the UEA NO_{xy} instrument on the BAe-146 that thermally converts NO_y to NO₂, using a gold convertor, photolytically converts NO₂ to NO and measures NO by chemiluminescence (Brough et al., 2003; Stewart et al., 2008). The instrument has detection limits of 3, 15 and 10 pptv and precisions of 10, 30 and 21% for NO, NO₂ and NO_y respectively.

Information regarding VOCs comes from the 15 min whole air samples (WAS) on board the BAe-146 which were analysed on the ground by dual-channel gas chromatography and flame ionization detection (Hopkins et al., 2003). The VOC detection limits and precisions varied from 1–10 pptv and 1–3%, respectively, depending on compound. Isoprene, acetone and the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) were also measured by proton mass transfer mass

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spectrometry (PTR-MS) at a higher time resolution and frequency (Table 1), but with detection limits of 20–80 pptv and 10% precision. PAN was measured by gas chromatography (30 pptv detection limit and 3% precision).

O₃ and NO₂ photolysis frequencies ($j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$) were measured on board the BAe-146 using 4 π sr filter radiometers (see Table 1). A 4 π sr $j(\text{NO}_2)$ radiometer (Meteorology Consult, GmbH, Glasshütten, 10% accuracy) was also used on board the D-Falcon.

3 Supporting calculations or modelling

Model calculations have been made using the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) (Emmerson and Evans, 2009; Stone et al., 2010). DSMACC is a zero-dimensional box model using the Kinetic Pre-Processor (KPP) (Sandu et al., 2006), constrained to observations of long-lived species with a chemistry scheme generated by the Master Chemical Mechanism (MCM) (Saunders et al., 2003).

A full description of the model calculations undertaken for the AMMA campaign can be found in Stone et al. (2010). To be modelled, time points needed to have observations of HO₂ or RO₂ together with the physical state (latitude, longitude, pressure, temperature and water vapour) and observations of CO, O₃, NO, $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$.

Observations of ethane, propane, *iso*-butane, *n*-butane, ethene, propene, acetylene, methanol, ethanol, acetone, formaldehyde, PAN, methyl ethyl ketone (MEK), isoprene, methyl vinyl ketone (MVK) and methacrolein (MACR) were also included where available and kept constant at the observed value. All observations used as input to the model were made on the BAe-146.

Concentrations of methane and hydrogen were kept constant at values of 1770 ppmv and 550 ppmv respectively. Where observations of alkanes and alkenes were not available, concentrations were estimated as a linear function of the CO concentration (Stone et al., 2010).

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For each time point, those species which have not been observed are set initially to zero. Those species which have been observed are set to the observed value and kept constant. However, concentrations of oxides of nitrogen are treated differently to other species in the model. For each time point during a day the concentration of NO_x (defined as $\text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \text{N}_2\text{O}_5 + \text{HONO} + \text{HNO}_4$) is corrected so that the total NO_x concentration is kept constant, but the concentration of the NO_x species varies owing to changes in photolysis rates etc. At the end of each day the calculated concentration of one of the NO_x species (typically either NO or NO_2) is compared to the equivalent measured concentration and the concentration of all NO_x species is fractionally increased or decreased so that the measured and the modelled concentrations of the observed species match.

Photolysis rates in the model are calculated from TUV, assuming a constant ozone column of 260 Dobson units and an albedo of 0.1. Cloud correction factors for all reactions other than $\text{O}_3 \rightarrow \text{O}(^1\text{D}) + \text{O}_2$ are calculated from the ratio of observed to simulated $j(\text{NO}_2)$, with the cloud correction factor for $\text{O}_3 \rightarrow \text{O}(^1\text{D}) + \text{O}_2$ calculated from the ratio of observed to simulated $j(\text{O}(^1\text{D}))$.

A removal reaction was included for all species which can be considered as a continuous deposition process (such as dry deposition or continuous wet deposition). The deposition lifetime was initially set at 24 h and the sensitivity investigated.

For each observation of HO_2 or RO_2 the objective is to calculate an expected value from the other parameters measured on board the aircraft and the chemical scheme used. All aircraft parameters have been merged onto a 60 s timebase for expediency. The model is integrated forward in time with diurnally varying photolysis rates until a steady state is reached when the fractional difference in mean species concentration between a day and the previous day is less than 0.01. Full details can be found in Stone et al. (2010).

4 Discussion of results

Figure 2 shows the peroxy radicals measured by the DUALER, PERCA 4 (RO_2^*) and FAGE (HO_2) at the two pressure levels of the intercomparison exercise. As explained in Sect. 2.2.2, a relative humidity correction was applied to the PERCA 4 data set [RO₂-PERCA 4] but this lead to spuriously high concentrations. [RO₂-PERCA 4] are only available for the first pressure level measured (697 hPa) owing to a loss of sample airflow at the higher altitude. As can be seen in Fig. 2, within this level [RO₂*] vary between 15 and 35 pptv and [HO₂] between 18 and 20 pptv. If the humidity correction is not applied, [RO₂-PERCA 4] and [RO₂*-DUALER] agree within their respective errors, otherwise [RO₂-PERCA 4] is significantly greater. At the second pressure level (485 hPa), the variability of [RO₂*-DUALER] increases although the range of concentrations remains generally between 15 and 45 pptv. There is no indication of any experimental artefact related to the 45 pptv [RO₂*-DUALER] measured at the beginning of the layer. This apparent outlier mixing ratio agrees temporally with short term peak variations of other trace gases measured (acetone, CO, O₃).

For this leg [HO₂] varies within and 6 and 18 pptv and the temporal variation shows two abrupt steps at 15:35 and 15:42 h. Both of these steps follow periods where the laser wavelength is rescanned to the maximum of the OH rotational line. This rescanning process takes ca. 2 min and no ambient data are collect during this procedure. Laser diagnostic measurements of power and wavelength stability during the three HO₂ measurement periods in this leg show there is no evidence to suggest that the instrument sensitivity has undergone a change and it is concluded that the two steps in the HO₂ concentration are real variations.

Interestingly, the variations of [RO₂*-DUALER] and [HO₂] do not agree temporally, in particular for the flight period between 15:35–15:45 h. As the [HO₂] remains very even, the [RO₂*-DUALER] seems to mirror a change in the radical partitioning of the air mass sampled in favour of organic peroxy radicals.

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In principle, the atmospheric radical variability is driven by radiation and/or other trace gas variability. Therefore, the radical temporal evolution observed during the flight was compared with the variability of the photolysis frequencies and radical precursors measured simultaneously.

5 4.1 Photolysis rates

Measurements of $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ are presented in Fig. 3. There is no BAe-146 data for the second intercomparison level as the field of view of the downward facing radiometers were obscured owing to the deployment of a protective shutter.

$j(\text{O}^1\text{D})$ was not measured on board the D-Falcon. At 697 hPa, a systematical difference between $j(\text{NO}_2)$ radiometers on both aircrafts was identified (see Fig. 3). While the downward facing $j(\text{NO}_2)$ radiometers show very good agreement, the D-Falcon upward $j(\text{NO}_2)$ radiometer is about 25% systematically higher than the BAe-146 upward facing sensor at both pressure levels. According to Volz-Thomas et al. (1996), temperature variations between 25 and -40°C can only account for 2–3% changing in the instrument sensitivity. The calibrations of the upper and lower $j(\text{NO}_2)$ radiometers in the BAe-146 before and after AMMA are consistent with one another having both been referenced to the Tropospheric Ultraviolet and Visible radiation model (TUV, <http://cprm.acd.ucar.edu/Models/TUV/>). Calibrations of the D-Falcon sensors are in preparation for clarifying the origin of the observed discrepancies.

The temporal variations observed in $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ agree qualitatively with the decrease in radical production measured between 15:05 and 15:10 h at 697 hPa but do not correlate at all with the variability observed at 485 hPa.

4.2 Radical related trace gases

Concerning other related trace gases, NO and NO_x remain around the detection limit. Both NO_y (D-Falcon) and PAN (BAe-146) are significant higher at 485 hPa (Stewart et al., 2008) as are CO_2 (not shown, $\Delta\text{CO}_2 \sim 1$ ppm), CO and O_3 . The $[\text{RO}_2^* \text{-DUALER}]$

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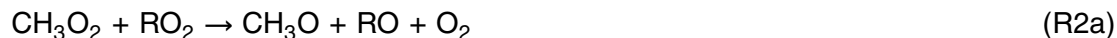
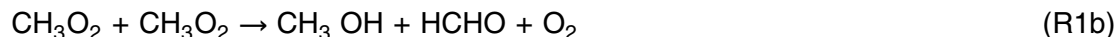
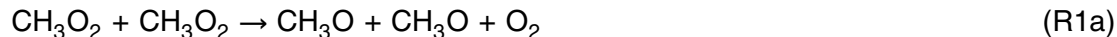
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variations closely follow the changes in [CO] between 15:30 and 15:50 h (Fig. 4), the minimum in the [CO]/[O₃] ratio at 15:45 indicating horizontal advection of an air mass enriched in CO rather than vertical convection, as [CO] remains lower in the previous higher altitude run at 697 hPa.

Acetone measured by PTR-MS shows minor short term variations in both pressure levels, and similarly to the HCHO measured on board the D-Falcon decreases slightly at 495 hPa on average from 1 ppbv to 0.8 ppbv. The corresponding WAS results indicate more marked peak concentrations at 15:30 in acetone and also in acetaldehyde which likely result from the integration related to the lower time resolution of the WAS samples.

Isoprene and its oxidation products methyl vinyl ketone and methacrolein (not shown) remain low and relatively constant, not indicating any recent influence of biogenic VOC.

Owing to the strong altitude dependence on the sampling and zeros reported by Murphy et al. (2010) during the AMMA measurement campaign, no PTR CH₃OH data are available for the intercomparison period. The GC analysis of the WAS samples at lower time resolution shows a significant CH₃OH maximum (1.6 ppbv) at the beginning of the first pressure level (around 15:00 h) and an increase from 0.3 to 0.5 ppbv between 15:30 and 15:35 h at 485 hPa. Similarly, MEK increases from 0.05 to 0.7 ppbv at 15:35 h. MEK is an indicator of industrial and gasoline engine emissions, and its major sink is the reaction with OH producing acetaldehyde. Apart from biogenic emissions, CH₃OH is produced by reaction of the methylperoxy radical with itself and other organic peroxy radicals (Madronich and Calvert, 1990; Tyndall et al., 2001):



The HCHO measured on board the D-Falcon increases concurrent to CH₃OH from 350 to 385 pptv. This can be considered as an upper limit of the CH₃OH which can be attributed to Reaction (R1b). Other minor sources of methanol are biomass burning and biofuels and fossil fuel combustion and industrial activities, as in the case of MEK. Acetonitrile and benzene do not provide any indication of recent biomass burning influence in the air mass.

Summarising, the variability of the trace gases measured at the second pressure level of the intercomparison exercise indicate changes in the composition of the air mass sampled which can reasonably be correlated to the variability of the local peroxy radicals measured.

4.3 Radical partitioning

Figure 5 shows the ratio ($[RO_2^* \text{-DUALER}]/[HO_2]$) for both measured levels. At 697 hPa, both the variability of the measured mixing ratios and the number of HO₂ measurements available is smaller and the ratio seems to remain quite stable around 2.5. This ratio is more scattered at 485 hPa, remaining between 1 and 3 as result of the variability of $[RO_2^*]$ discussed above. There are only a few $[RO_2^*]/[HO_2]$ values reported for the upper troposphere (1.86: Cantrell et al, 2003a; 1.25: Cantrell et al., 2003c). It is important to emphasise that $[RO_2^*]/[HO_2]$ is not expected to be constant but to be directly related to the NO and VOC content and history of the air mass sampled.

A similar comparison between $[HO_2]$ and $[RO_2^*]$ measured by LIF and Chemical Ionisation Mass Spectrometry (CIMS) respectively was undertaken within the TRACE-P measurement campaign (Eisele et al., 2003; Cantrell et al., 2003a, b). The $[RO_2^*]$ versus $[HO_2]$ average data, are quite scattered as expected since the $[RO_2^*]/[HO_2]$ ratio is not necessarily constant during the three sets of intercomparison flights, but can reasonably be fitted by a slope of 2.46.

The CL of the DUALER measured in the laboratory is an effective CL (eCL) coming from the chain reaction of the radicals not being lost in the pre-reactor nozzle. As the peroxy radicals are reacting rapidly with the walls, the losses at this nozzle before

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the addition of CO and NO are expected to be important. According to the laboratory characterisation of the response of the DUALER for different peroxy radicals (Kartal et al., 2010), higher eCL is to be expected for CH₃O₂ than for HO₂ as a consequence of lower wall losses of CH₃O₂ in the pre-reactor nozzle. Using a common eCL for the determination of [RO₂^{*}] in ambient samples as during AMMA can cause an overestimation depending on the [HO₂]/[CH₃O₂] ratio. The [RO₂]/[HO₂] ratios vary mostly between 1:1 and 2:1 during the intercomparison exercise and CH₃O₂ is expected to constitute 88% of the total organic peroxy radicals (see Sect. 4.4). Under these conditions the experimental [RO₂^{*}-DUALER] reported in this work might be 8 to 16% overestimated.

Radical partitioning over the whole AMMA campaign derived from the simultaneous measurement of [RO₂^{*}] and [HO₂] on board the BAe-146 is discussed more in detail in Brookes (2010).

4.4 Modelling of radical concentrations

Comparisons between modelled [HO₂] and [RO₂^{*}] with observations are shown in Figs. 6–8. As mentioned above, HO₂ was only partially measured at 697 hPa and RO₂^{*}-PERCA 4 is completely unavailable for the second intercomparison period. This reduces drastically the statistics and representativeness of the results obtained within the intercomparison exercise.

At a first glance the model results in Fig. 6 seem to generally overestimate [HO₂] during the intercomparison exercise, which results in some overprediction of total modelled [RO₂^{*}]. It is possible that flying adjacent to the D-Falcon may have had some effect on the flow conditions within the FAGE inlet, resulting in greater loss of HO₂ in the inlet and reduced HO₂ detection compared to calibration conditions, although such effects have not been reported in previous aircraft HO_x intercomparison exercises (Eisele et al., 2003). This might partly explain the stepwise temporal evolution of [HO₂] observed at 485 hPa.

It is important noting that the use of the model in particular for the AMMA intercomparison period is subject to important restrictions derived from following issues:

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(a) Photolysis rates:

As described in Sect. 3, the DSMACC model requires observations of $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$, which were not available for the second altitude level. The existing discrepancies between $j(\text{NO}_2)$ measured on board the BAE-146 and D-Falcon prevent the direct use of the $j(\text{NO}_2)$ -D-Falcon data for the 485 hPa pressure level without introducing unknown uncertainties. Model runs using $j(\text{NO}_2)$ -D-Falcon show higher radical concentrations than model runs constrained to photolysis rates measured on the BAe-146 as expected since the $j(\text{NO}_2)$ -D-Falcon measurement is systematically 25% higher than the $j(\text{NO}_2)$ -BAe-146 measurement (see Fig. 3). Scaling of the $j(\text{NO}_2)$ -D-Falcon to the values observed on the BAe-146 gives similar results to model results constrained to the BAe-146 photolysis results, and provides some additional data points during the second intercomparison period (Fig. 7). The agreement between $[\text{HO}_2]$ modelled and measured improves and the modelled $[\text{RO}_2^*]$ for the second period show good agreement on the average with the observed $[\text{RO}_2^*\text{-DUALER}]$ though the short term variability of the observations is not completely picked up (Fig. 8)

Concerning $j(\text{O}^1\text{D})$, the BAe-146 measurements may have been subject to a systematic bias derived from the non-linearity of $j(\text{O}^1\text{D})$ calibration factors for total O_3 column, temperature and solar zenith angle, as described in Stone et al. (2010) and Brookes (2009). This results in a potential requirement for reduction in $j(\text{O}^1\text{D})$ by a factor of 0.7. The bias appears more significant at altitudes above 4 km where the impact of cloud and aerosol is much reduced. A similar correction to the $j(\text{O}^1\text{D})$ in the model did result in a lowering of the modelled HO_2 , and although the reduction in $j(\text{O}^1\text{D})$ rectifies much of the overestimation for HO_2 in the model, it was not sufficient to explain the model discrepancy during the intercomparison period.

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(b) Input of trace gas observations:

There are a limited number of VOC observations at high temporal resolution during the intercomparison period. As the input for the model is updated every 60 s, the use of WAS samples with 15 min resolution can introduce unrealistic stepwise significant variations in the mixing ratio of trace gases. In addition, as reported on Reeves et al. (2010) the HCHO measured on board the BAe-146 showed unrealistic oscillations during the intercomparison exercise. Figure 9 compares the HCHO output of the model with the HCHO measured on board the D-Falcon. Furthermore, as the NO_x mixing ratios remained below the detection limit of the instruments deployed, the comparison of the model with a reliable experimental reference as described in Sect. 3 is not possible.

The importance of some of these issues in the application of box models to observationally based predictions of HO_x radicals has been recently evaluated by Olson et al. (2004, 2006). The present work intends to focus on the analysis of the uncertainties of experimental data rather than on the comparison with model results. Given the limitations described above and the inherent challenges of the airborne radical measurement and modelling, the overestimate of HO₂ during the intercomparison period does not appear to be an indication of an inability in the model to replicate observations of HO₂. In fact there is no significant overestimation of measured [HO₂] for the modelling of the AMMA campaign as a whole, as discussed in Stone et al. (2010) and summarised in Fig. 10.

Rates of production/destruction analyses (ROPAs/RODAs) for the model run using photolysis rates measured on the BAe-146 indicates that the dominant reactions responsible for HO₂ production during the intercomparison periods were OH+CO (39%), CH₃O+O₂ (15%), HCHO+OH (10%) and HCHO photolysis (9%). While individual contributions to HO₂ production from RO+O₂ reactions are relatively small, they do contribute significantly to the remainder of the total.

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Dominant loss processes for HO₂ were HO₂+NO, comprising 35% of the total loss, HO₂+HO₂ (28%), HO₂+CH₃O₂ (11%) and O₃+HO₂ (8%). Cycling of HO₂ between the HO₂ and HO₂NO₂ was also a significant process during the intercomparison periods, and reactions of HO₂ with RO₂ species also contributes significantly to the total HO₂ loss.

The dominant peroxy species in terms of HO₂ loss were also the most abundant RO₂ species in the model, with CH₃O₂ constituting 88% of the total organic peroxy radical concentration. A more detailed RO₂ speciation from the model is given in Table 2.

5 Summary and conclusions

The measurement of peroxy radicals requires the use of very sensitive and well calibrated measurement techniques. Owing to the particular complexity of airborne measurements, any laboratory characterisation must however be accompanied by in flight intercomparisons and calibrations of the instrumentation in order to identify malfunctions under field conditions and to prevent biases in the analysis of results.

In that context, the radical intercomparison exercise within AMMA intends for the first time to compare the performance of a LIF-FAGE, measuring [HO₂], and two similar PerCA instruments, measuring the total sum of peroxy radicals [RO₂*], deployed in two different aircrafts and sampling at two pressure levels over the same geographical area.

Some instrumental failures limited the number of data available for comparison. Nevertheless the results obtained provide very valuable information for the analysis of the AMMA campaign as a whole:

- (a) [RO₂-PERCA 4] and [RO₂*-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 [RO₂-PERCA 4] corrected data set

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remains unrealistically higher. This supports the conclusion that it is inappropriate to use the humidity corrected data from the PERCA 4 instrument for the rest of the AMMA campaign.

(b) The response of the $j(\text{NO}_2)$ radiometer on board the D-Falcon remains systematically higher than the equivalent radiometer on the BAe-146. There is a systematic 25% difference in the upward facing sensors at both pressure levels. This emphasises the importance of specific calibrations and verification of 2π sr radiometers to prevent spuriously simulation of radical mixing ratios, as confirmed by the sensitivity study undertaken with the DSMACC model. These discrepancies require exercising caution when comparing model results from the two aircrafts.

Concerning the content of the air masses sampled, the radical mixing ratios vary on the average between 7 and 20 pptv for $[\text{HO}_2]$ and 15 and 40 pptv for $[\text{RO}_2^*]$ at both pressure levels. The $[\text{RO}_2^*]$ variability increases significantly at the higher pressure level (485 hPa) indicating input of precursors of organic peroxy radicals, in reasonable agreement with other trace gas observations. The existence of a layer photochemically active at this altitude has been reported during AMMA (Andrés-Hernández et al., 2009; Reeves et al., 2010). The $[\text{RO}_2^*]/[\text{HO}_2]$ ratios vary between 1:1 and 3:1 and seem to be more stable and closer to the expected 2:1 for remote areas at the lower pressure level (697 hPa). According to the laboratory characterisation of the DUALER (Kartal et al., 2010), using a common chain length for the $[\text{RO}_2^*]$ determination during the intercomparison exercise can lead to an 8–16% overestimation of the reported $[\text{RO}_2^* \text{-DUALER}]$.

The results of this intercomparison campaign confirm the necessity of additional effort to improve not only the in-flight cross calibration of airborne measurements for peroxy radicals but also the rapid and high sensitive measurement of photolysis rates and other associated species like VOCs and NO, which play a central role in the discrimination between unexpected experimental malfunctions and unknown atmospheric chemistry. Furthermore, the broad and accurate knowledge of instrumental limitations

and potential artefacts in the field is indispensable for the correct use of airborne measurements of short lived species for the modelling of local photochemistry.

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Table 1. Summary of the measurement techniques deployed during the AMMA peroxy radical intercomparison exercise, $[RO_2^*] = ([HO_2] + \sum [RO_2])$; dl: detection limit.

Instrument/ Aircraft	Technique	Measurement	Institution	Time resolution	Special features
DUALER/ D-Falcon	PerCA	$[RO_2^*]$	IUP-UB	1 s, 60 s reported	Dual inlet, P controlled, HO_2 calibration
PERCA 4/ BAe-146	PerCA	$[RO_2^*]$	University of Leicester	1 s, 60 s avg	Dual inlet, CH_3O_2 calibration
BAe-146	FAGE	HO_2 by titration to OH	University of Leeds	1 s, 60 s reported	Commene et al., 2010
UV photometer/ D-Falcon	UV absorption	O_3	DLR	1 s, 5% accuracy	dl: 1 ppb
Aerolaser AL5002/ D-Falcon	VUV fluorescence	CO	DLR	1 s, 3% accuracy	dl: 1 ppb
NR-IR photometer/ D-Falcon	IR absorption	CO_2	DLR	1 s, 0.3 ppm accuracy	dl: 0.1 ppm
Whole Air Samples (WAS)/ BAe-146	off line analysis with dual channel GC	VOCs	University of York	15 min	Grab samples
NO_x - NO_y / D-Falcon	Phot. convert- NO_2 Au- convertor- NO_y Chemilumin. (NO)	NO_y , NO	DLR	1 s	dl: 5 pptv (NO) 15 pptv (NO_y)
/BAe-146	Gas Chromatography	PAN	University of Leeds	90 s	
YES, Inc, AL4021/ D-Falcon	Hantzsch technique, Fluorometry	HCHO	DLR	60 s, 15% accuracy	dl<50 pptv
Ionico Analytik/ BAe-146	Proton Transfer Mass Spectrometer (PTR-MS)	Real-time Oxygenates	University of East Anglia	1–2 s	Every 15 s
/BAe-146	Filter radiometry	$j(NO_2)$	University of Leicester	1 s	4π sr
/BAe-146	Filter radiometry	$j(O^1D)$	University of Leicester	1 s	4π sr
/D-Falcon	Filter radiometry	$j(NO_2)$	DLR	1 s	4π sr

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Table 2. Organic RO₂ speciation from DSMACC during the intercomparison period. Species names are from the MCM. Note that ISOPAO₂, ISOPBO₂, ISOPDO₂, C57O₂, C58O₂, C59O₂, HMVKAO₂, HMVKBO₂ and MACRO₂ are all derived from isoprene and its oxidation products.

RO ₂	% to total organic RO ₂ concentration
CH ₃ O ₂	87.96
ISOPBO ₂	2.50
CH ₃ CO ₃	2.01
CH ₃ COCH ₂ O ₂	1.08
C ₂ H ₅ O ₂	0.89
HOCH ₂ CO ₃	0.75
C59O ₂	0.65
HMVKBO ₂	0.62
MACRO ₂	0.58
ISOPDO ₂	0.41
C58O ₂	0.36
C57O ₂	0.29
ISOPAO ₂	0.26
HMVKAO ₂	0.26
Remaining	1.38

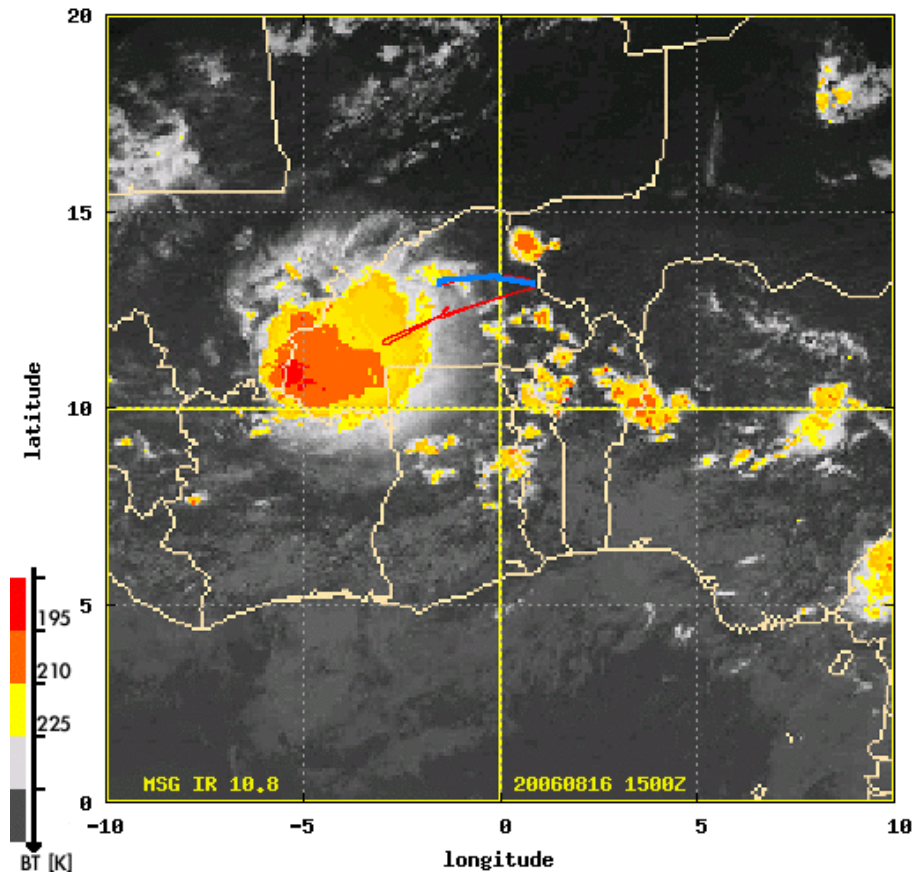


Fig. 1. Flight track on 16 August 2006. The part corresponding with the AMMA intercomparison exercise is highlighted in blue and was from 15:00 to 15:50 whilst the Meteosat infrared image is from 15:00 UTC.

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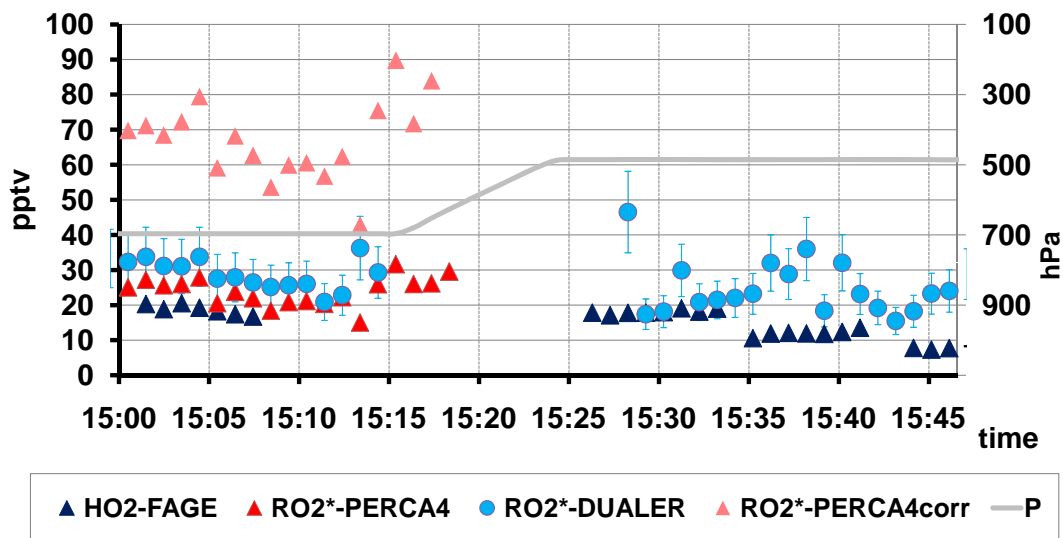
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Fig. 2. Peroxy radicals measured during the AMMA intercomparison exercise. The pressure at the two measurement levels is indicated in grey. RO_2^* -PERCA4corr are the $[\text{RO}_2^*]$ obtained by applying the relative humidity correction of the CL to the PERCA 4 instrument.

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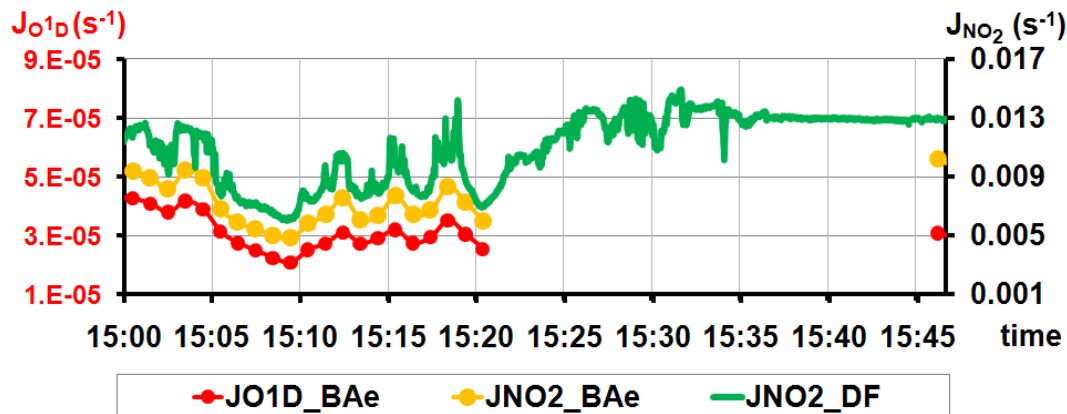


Fig. 3. Temporal variability of the photolysis rates measured during the AMMA intercomparison exercise. DF stands for D-Falcon and BAe for BAe-146.

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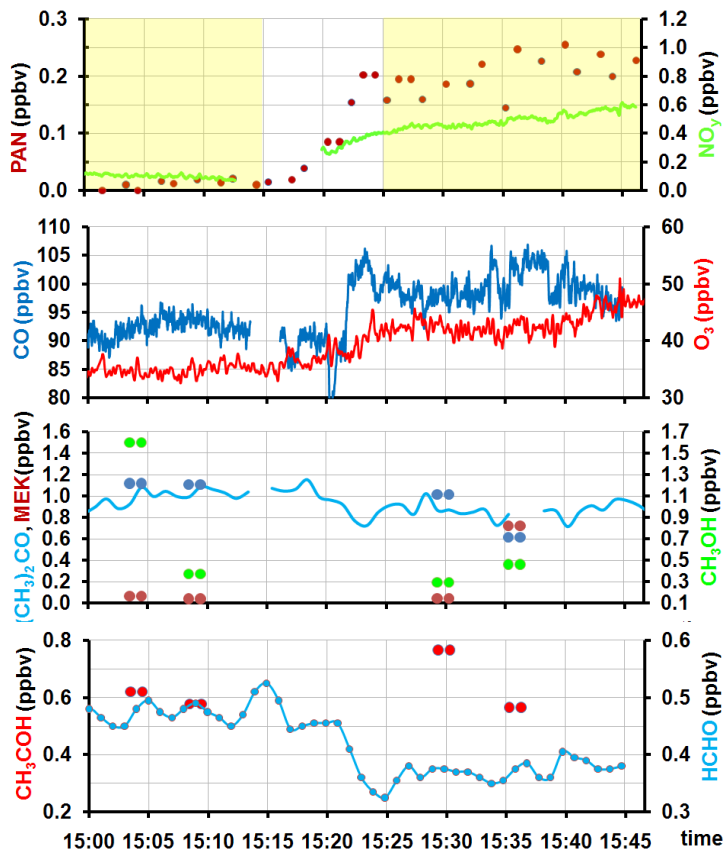
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Fig. 4. Variation of related trace gases during the AMMA radical intercomparison exercise: CO, O₃, NO_y, and HCHO as measured on board the D-Falcon, (CH₃)₂CO, CH₃COH, MEK, PAN and CH₃OH as measured on board the BAe-146. The (CH₃)₂CO measured by PTR-MS (blue line) agree reasonably with the WAS samples (blue dots). The periods of the intercomparison are highlighted in the top figure in yellow.

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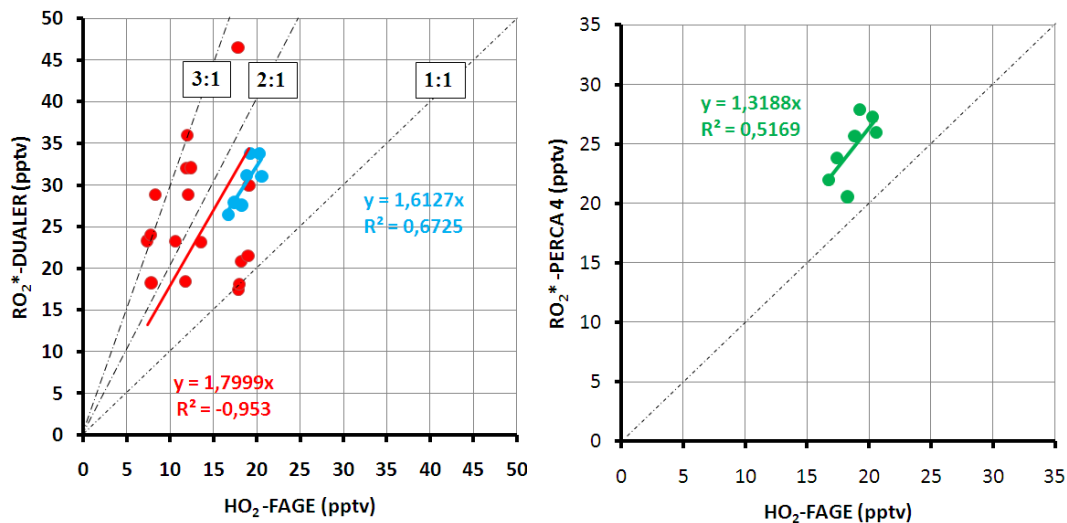


Fig. 5. $[\text{RO}_2^*]/[\text{HO}_2]$ ratio measured during the AMMA intercomparison exercise. In blue and green are the data corresponding to the first pressure level measured (697 hPa).

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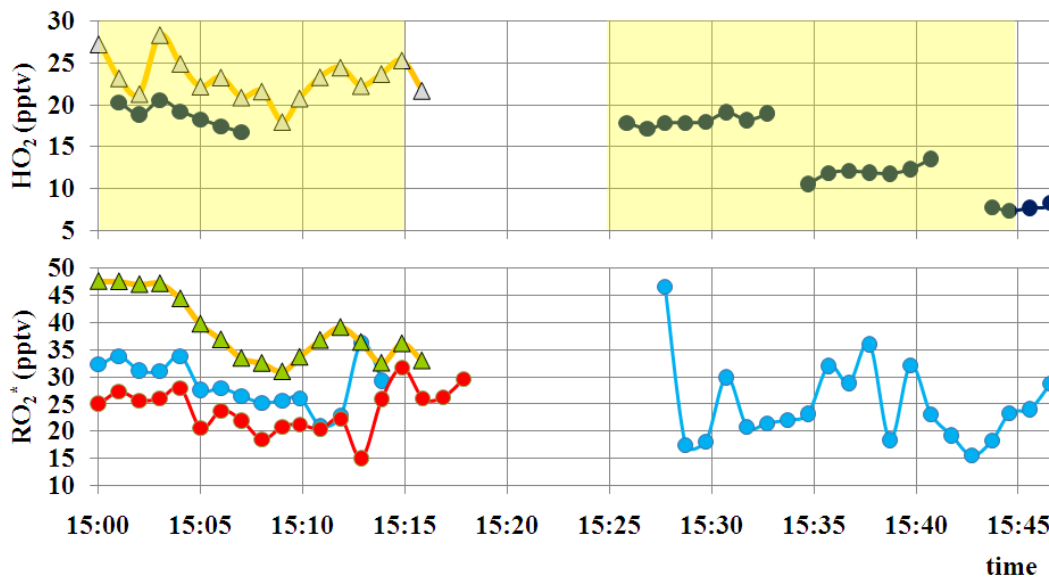


Fig. 6. Comparison of model and observations ($[\text{HO}_2\text{-FAGE}]$ in dark blue, $[\text{RO}_2^*\text{-DUALER}]$ in blue and $[\text{RO}_2^*\text{-PERCA 4}]$ in red) for the 697 hPa pressure level during the intercomparison exercise. Model results (triangles) are constrained to $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ measured on board the BAE-146. The periods of the intercomparison are highlighted in the top figure in yellow.

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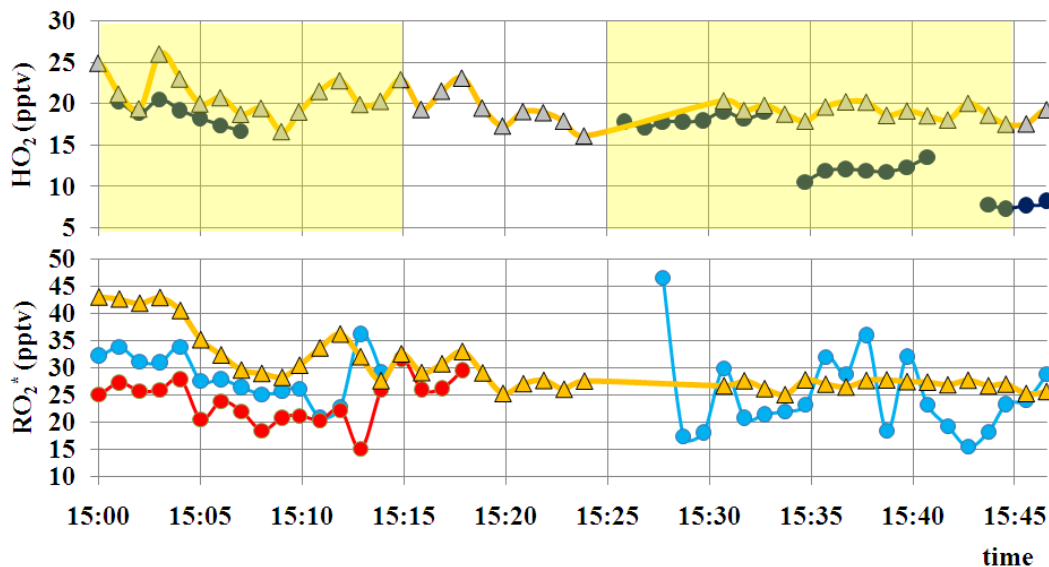


Fig. 7. Comparison of model and observations ($[\text{HO}_2]$ in dark blue, $[\text{RO}_2^* \text{-DUALER}]$ in blue and $[\text{RO}_2^* \text{-PERCA 4}]$ in red) for the 697 hPa pressure level during the intercomparison exercise. Model results (triangles) are constrained to $j(\text{NO}_2)$ measured on board the D-Falcon scaled to the $j(\text{NO}_2)$ -BAe values measured at 697 hPa. The periods of the intercomparison are highlighted in the top figure in yellow.

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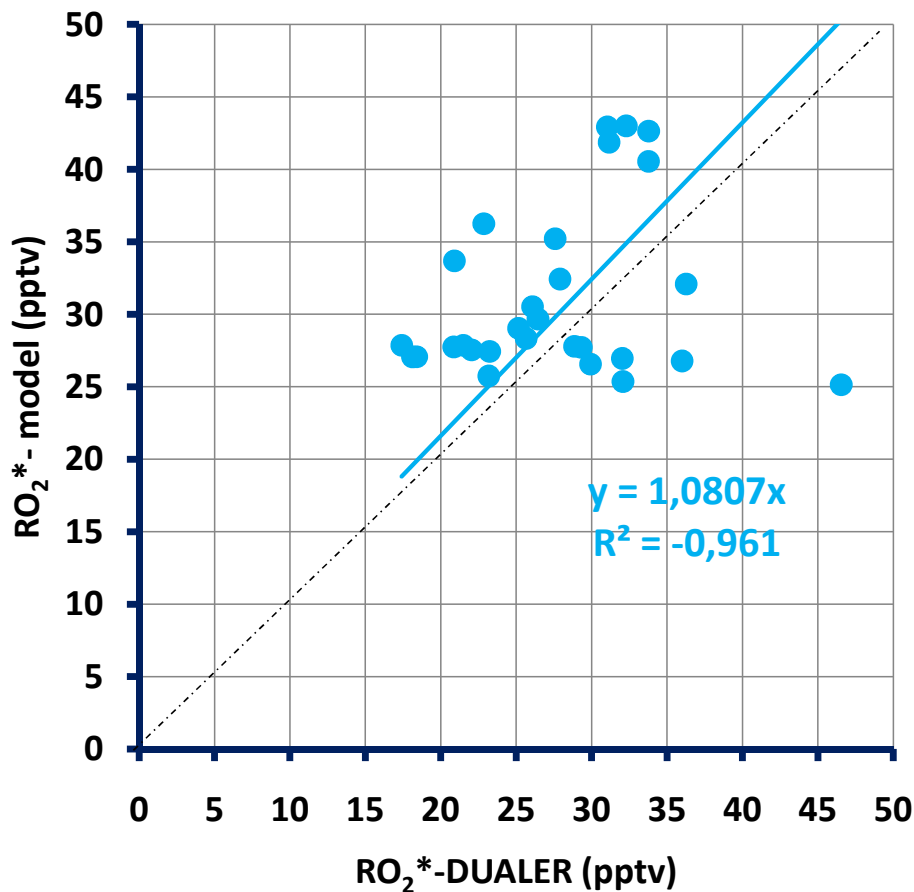
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Fig. 8. $[\text{HO}_2 + \text{RO}_2]$ model versus $[\text{RO}_2^*]$ observations on board the D-Falcon for both altitudes during the AMMA intercomparison exercise. The model is constrained to $j(\text{NO}_2)$ measured on board the D-Falcon scaled to the $j(\text{NO}_2)$ -BAe values measured at 697 hPa.

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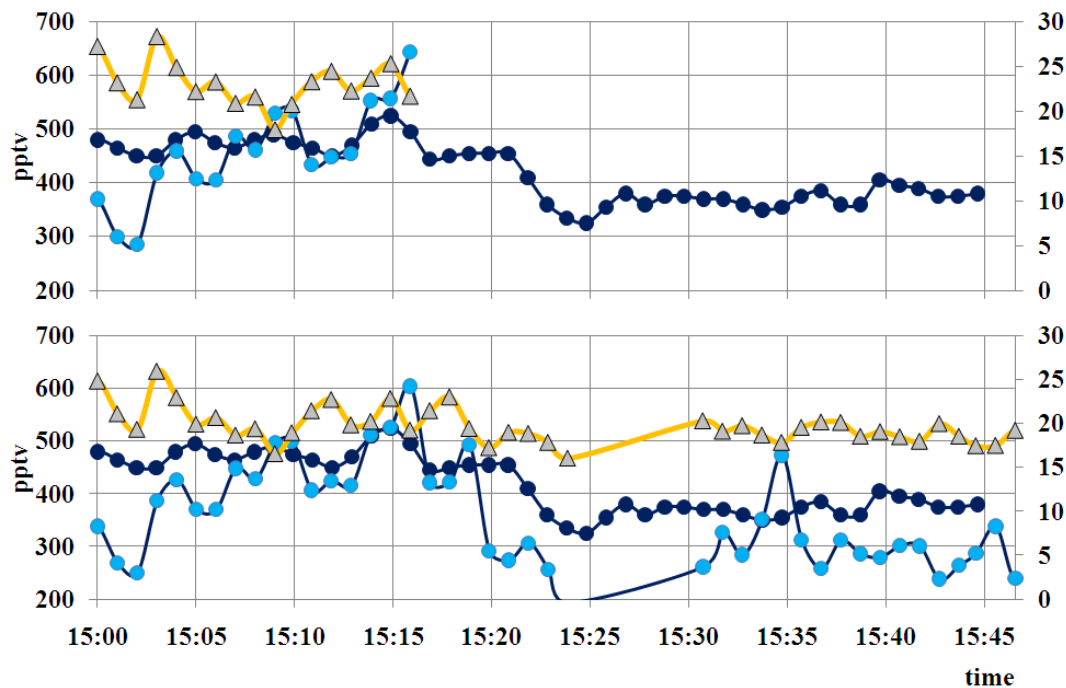
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Fig. 9. [HCHO] measured on board the D-Falcon (dark blue circles) and modeled (blue) for the intercomparison exercise. The model data are constrained as in Figs. 6 and 7. The corresponding [HO₂] model data are also included for comparison.

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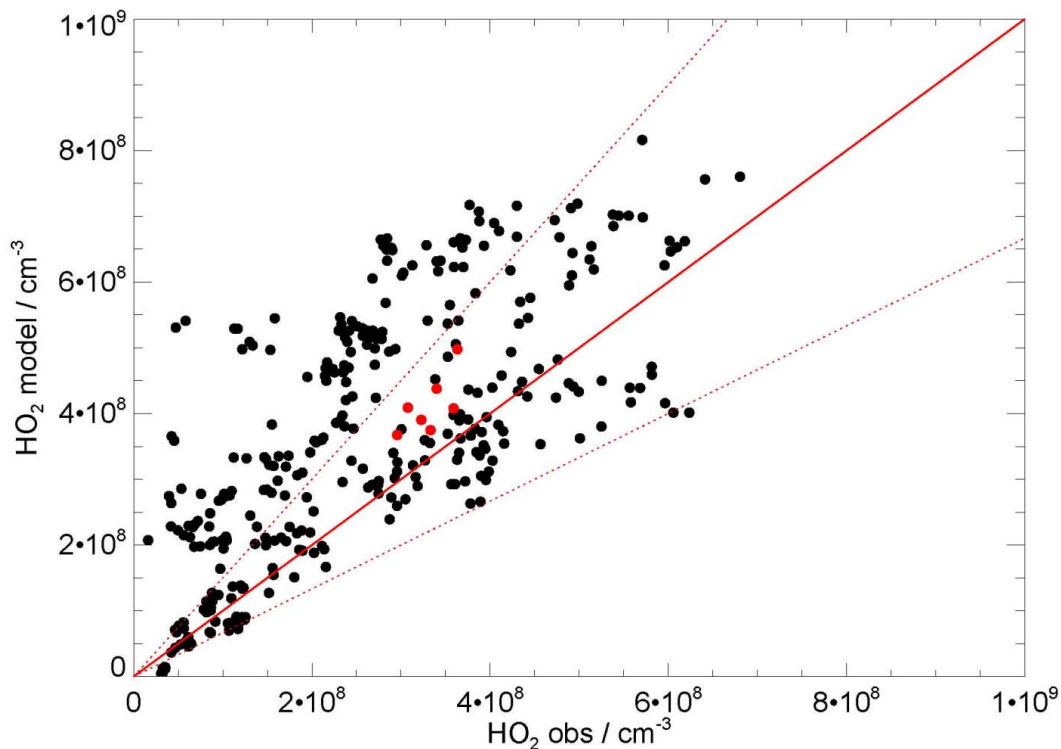
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Fig. 10. Comparison between HO₂ modeled and observed concentrations using measurements made on board the BAe-146. In red are the data corresponding with the intercomparison period.

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