

Observations of OH and HO₂ radicals over West Africa

R. Commane^{1,*}, C. F. A. Floquet^{1,**}, T. Ingham^{1,2}, D. Stone^{1,3}, M. J. Evans³, and D. E. Heard^{1,2}

¹School of Chemistry, University of Leeds, LS2 9JT, UK

²National Centre for Atmospheric Science, University of Leeds, LS2 9JT, UK

³Institute for Climate & Atmospheric Science, School of Earth & Environment, University of Leeds, LS2 9JT, UK

* now at: School of Engineering & Applied Sciences, Harvard University, Cambridge, USA

** now at: National Oceanography Centre, University of Southampton, Southampton, UK

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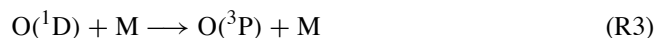
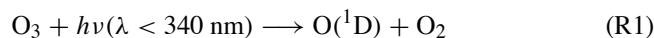
Abstract. The hydroxyl radical (OH) plays a key role in the oxidation of trace gases in the troposphere. However, observations of OH and the closely related hydroperoxy radical (HO₂) have been sparse, especially in the tropics. Based on a low-pressure laser-induced fluorescence technique (FAGE – Fluorescence Assay by Gas Expansion), an instrument has been developed to measure OH and HO₂ aboard the Facility for Airborne Atmospheric Measurement (FAAM) BAe-146 research aircraft. During the African Monsoon Multidisciplinary Analyses (AMMA) campaign, observations of OH and HO₂ (HO_x) were made in the boundary layer and free troposphere over West Africa on 13 flights during July and August 2006. Mixing ratios of both OH and HO₂ were found to be highly variable, but followed a diurnal cycle: OH varied from 1.3 pptv to below the instrumental limit of detection, with a median mixing ratio of 0.17 pptv. HO₂ varied from 42.7 pptv to below the limit of detection, with a median mixing ratio of 8.0 pptv. A median HO₂/OH ratio of 95 was observed. Daytime OH observations were compared with the primary production rate of OH from ozone photolysis in the presence of water vapour. Daytime HO₂ observations were generally reproduced by a simple steady-state HO_x calculation, where HO_x was assumed to be formed from the primary production of OH and lost through HO₂ self-reaction. Deviations between the observations and this simple model were found to be grouped into a number of specific cases: (a) within cloud, (b) in the presence of high levels of isoprene in the boundary layer and (c) within a biomass burning plume. HO₂ was sampled in and around cloud, with significant short-lived reductions of HO₂ observed. Up to 9 pptv of

HO₂ was observed at night, with HO₂ above 6 pptv observed at altitudes above 6 km. In the forested boundary layer, HO₂ was underestimated by a steady state calculation at altitudes below 500 m but overestimated between 500 m and 2 km. In a biomass burning plume, observed HO₂ concentrations were significantly below those calculated.

1 Introduction

The concentration of the hydroxyl radical (OH) determines the daytime oxidative capacity of the atmosphere. Reaction with OH is the major removal pathway for trace gases such as methane (CH₄), carbon monoxide (CO), Volatile Organic Compounds (VOCs) and some halocarbons, often as the first and rate-determining step in their oxidation. A deeper knowledge of the distribution of the concentration of OH and HO₂ (collectively known as HO_x) helps our understanding of atmospheric oxidation and fast photochemical processes.

Usually the primary production pathway of OH in the troposphere, $P(\text{OH})$, is through the photolysis of ozone (O₃) and the subsequent reaction of O(¹D) with water vapour (Ehalt, 1999):



The fraction of O(¹D) reacting with water vapour to produce OH (F_{OH}) rather than being quenched to O(³P) (R3) depends on the water vapour concentration present and is 0.1–0.15 in



Correspondence to: D. E. Heard
(d.e.heard@leeds.ac.uk)

typical boundary layer conditions. From this, the primary rate of OH production can then be calculated as:

$$P(\text{OH}) = 2 J(\text{O}^1\text{D}) [\text{O}_3] F_{\text{OH}} \quad (1)$$

OH is quickly converted to the hydroperoxy radical (HO₂) by reaction with CO (Weinstock, 1969):



The reaction of OH with VOCs produces peroxy radicals (RO₂), which, in the presence of NO (nitric oxide), leads to the formation of HO₂. NO is also important as it rapidly recycles HO₂ to form OH, allowing OH and HO₂ to be considered as a combined HO_x family. The ultimate fate of the HO_x radicals is the formation of water soluble species such as H₂O₂ (through HO₂ self reaction) or HNO₃ (through the reaction of NO₂ with OH under high NO_x conditions), both of which can be subject to wet or dry deposition.

Tropical regions with high levels of solar irradiation, and often high humidity, have the highest production rates of OH (Bloss et al., 2005). The presence of high concentrations of OH and large surface areas allow tropical regions to dominate global oxidation of long-lived species. The rate of oxidation of CH₄ by OH is also highly dependent on temperature and 80% of this important greenhouse gas is oxidised in the tropical troposphere (Bloss et al., 2005). The tropics also contain large regions of forest, which are a large source of global biogenic VOCs (Fehsenfeld et al., 1992; Guenther et al., 1995), with isoprene (C₅H₈) contributing about 40% of global VOC emissions (Guenther et al., 2006; Kesselmeier, 1999). Most biogenic emissions are controlled by solar irradiation and temperature (Kesselmeier, 1999; Fuentes et al., 2000). Global models calculate that over regions with high concentrations of biogenic VOCs, OH will be depleted compared to concentrations at similar latitudes (Poisson et al., 2000; von Kuhlmann et al., 2004; Lelieveld et al., 2002; Karl et al., 2007). While there have been some observations of HO_x in the mid-latitudes (e.g. Heard and Pilling, 2003, and references therein), observations in the tropics have been less extensive, with a distinct focus on the Pacific ocean and American continents. In tropical marine air, OH mixing ratios up to 0.8 pptv (parts-per-trillion, 10⁻¹² mol mol⁻¹) and HO₂ mixing ratios between 2 and 45 pptv were observed during the PEM-Tropics-A (Mauldin et al., 1999), PEM-Tropics-B (Tan et al., 2001) and INTEX-B (Mao et al., 2009) aircraft campaigns over the Pacific, while maximum OH and HO₂ mixing ratios of 0.37 pptv and 24 pptv respectively were observed at a surface site in the North Atlantic ocean (Whalley et al., 2009). Lelieveld et al. (2008) found that mixing ratios of OH and HO₂ observed in the presence of high concentrations of isoprene over the rainforests of Suriname were not depleted to the extent expected. OH mixing ratios up to 0.8 pptv and HO₂ mixing ratios up to 80 pptv were observed

(Martinez et al., 2010), much higher than calculated in modelling studies (Kubistin et al., 2008).

This paper presents airborne observations of OH and HO₂ radicals above the understudied tropical West African region. The observations were made using a Fluorescence Assay by Gas Expansion (FAGE) instrument flown aboard the BAe-146 as part of the AMMA (African Monsoon Multidisciplinary Analyses) Special Observation Period 2 (SOP-2) intensive in July and August 2006. The instrument and the associated calibration procedure are described in some detail (Sect. 2). The variation of HO_x with altitude is presented in Sect. 3 and is interpreted in terms of the changing chemical environment, detailed previously in Stewart et al. (2008), Capes et al. (2009) and Reeves et al. (2010). OH mixing ratios are compared to the primary production rate, while HO₂ mixing ratios are compared to a simple steady-state calculation. From these comparisons, a number of interesting cases were identified for further examination. These include observations of HO_x in the boundary layer over forested regions (Sect. 4.3), HO_x observations in a biomass burning plume (Sect. 4.4), HO₂ observed in and around cloud (Sect. 4.1) and HO₂ at night (Sect. 4.2). In an accompanying paper, Stone et al. (2010) compare the HO_x observations presented here with a comprehensive box model. A inter-comparison of HO₂ and peroxy radicals observed on two aircraft flying close together during AMMA is discussed in Andres-Hernandez et al. (2010).

2 Experimental

The Leeds Aircraft FAGE instrument was designed to be flown aboard the BAe-146 research aircraft operated by FAAM (Facility for Airborne Atmospheric Measurements).

Fluorescence Assay by Gas Expansion (FAGE) is an on-resonance low pressure laser-induced fluorescence technique for the measurement of OH and HO₂ (Hard et al., 1984). The strong A²Σ⁺(v'=0) ← X²Π_i(v''=0) Q₁(2) transition of an OH molecule is excited by radiation at λ≈308 nm and the subsequent fluorescence is also detected at λ≈308 nm. The fluorescence cell is maintained at low pressure (ranging from 1.5 Torr at 9 km to 2.5 Torr at sea level) to ensure the fluorescence from the OH molecule lasts longer than the laser excitation pulse, which allows for temporal gating of the fluorescence detection. OH and HO₂ are detected simultaneously with two excitation axes in series. After the OH detection axis, NO is added to the air flow to titrate HO₂ in the sample gas to OH, which is detected in the HO₂ axis.



The sensitivity of the instrument to OH and HO₂ must be determined by calibration. Figure 1 shows the instrument set-up. The instrumentation is installed on two 19 inch aircraft racks, located behind the fluorescence cell sampling point with pumps located below the fluorescence cell.

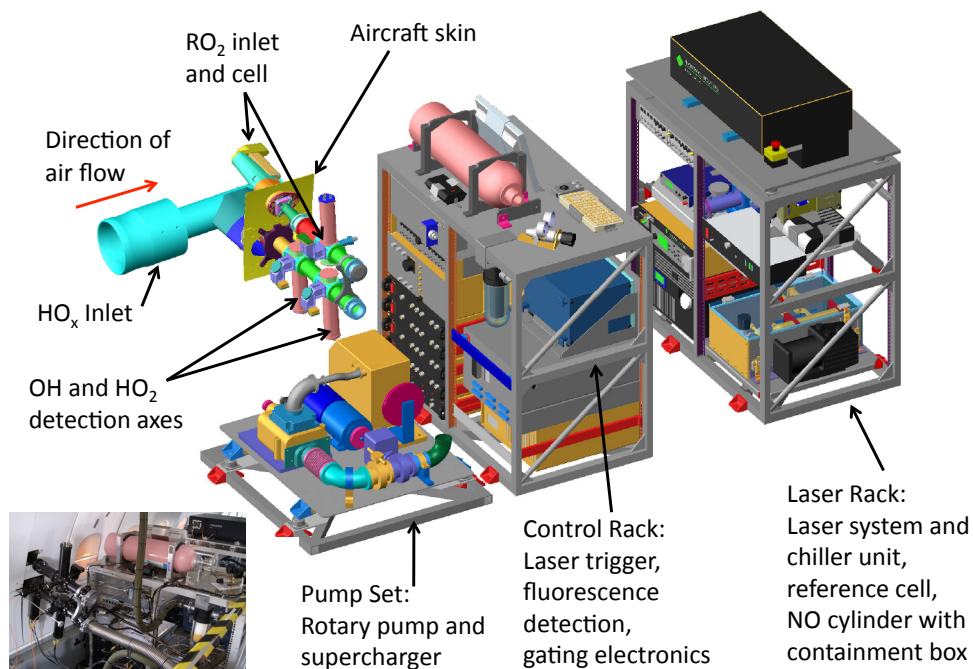


Fig. 1. Schematic outline of the Leeds aircraft FAGE instrument. Individual components are detailed in the text. The inlet delivers air to the fluorescence cell with OH and HO₂ detection axes. The cell is maintained at low pressure (1.5–2.1 Torr) by a rotary pump backed by a supercharger (Pump Set). The fluorescence cell and pump set are not joined for clarity. The Control Rack contains the instrument computer with photon counting cards, the photomultiplier power supplies and gating electronics, the laser trigger module and a nitrogen cylinder. The Laser Rack holds the YAG pumped Ti:Sapphire laser and chiller unit, the reference cell and a B2 size NO cylinder for HO₂ measurements. The NO cylinder is housed in a containment box designed to prevent any NO leak in the aircraft cabin in case of failure of the cylinder or regulator. Fibre optic cables (not shown) deliver the laser light from the laser to the OH, HO₂ and reference cells. An inlet and fluorescence cell for the detection of RO₂ have been fitted but are not yet operational.

2.1 HO_x radical sampling

Ambient air from outside the aircraft is sampled through an inlet (adapted from Eisele et al., 1997) mounted on a window blank on the starboard side of the BAe-146, close to the front of the aircraft. Using two concentric tubes with restrictions, the inlet slows the air prior to sampling, while minimising turbulence, and hence wall contact, and the associated loss of OH radicals.

Air is drawn in through a pinhole (0.75 mm diameter) to a fluorescence cell maintained at reduced pressure by a rotary pump (Leybold Trivac D25B) coupled with a supercharger (Eaton M90). In order to extend outside the aircraft skin and deliver OH to the excitation axis, a tube made of anodised aluminium (internal diameter = 5 cm; length = 50 cm) was added to the fluorescence cell. Characterisation tests on the cell have shown significant OH loss on contact with the internal tube walls, thus reducing the instrument sensitivity to OH. No solar scattered light has been detected at either the OH or HO₂ detection axes when the instrument was operated on the aircraft. A fluorescence cell for the detection of RO₂ is shown in Fig. 1 but is not yet operational.

2.2 Laser excitation of OH

Laser light at $\lambda \approx 308$ nm was generated by a laser system consisting of a Nd:YAG (Neodymium-ion doped Yttrium Aluminium Garnet (Y₃Al₅O₁₂) DS20-532, Photonics Industries) pumped Titanium Sapphire (Ti:Sapp) laser (TU-UV 308 nm, Photonics Industries). The YAG laser typically produces 9–10 W of light at $\lambda = 532$ nm at a Pulse Repetition Frequency (PRF) of 5 kHz, which is used to pump the Ti:Sapp laser. The Ti:Sapp output wavelength of $\lambda \approx 924$ nm is selected through the use of a diffraction grating and is passed through the first of two non-linear harmonic generation stages consisting of a Cerium Lithium Borate (CLBO) crystal, generating the second harmonic at $\lambda \approx 462$ nm. A half wave plate corrects the polarisation of the light to allow the second crystal to perform sum-frequency mixing of the second harmonic ($\lambda \approx 462$ nm) with the fundamental ($\lambda \approx 924$ nm), producing light at $\lambda \approx 308$ nm.

Under optimal conditions, ~ 100 mW of UV radiation is produced with a pulse width of 35 ns (Full Width Half Maximum, FWHM) and a laser linewidth of 0.065 cm⁻¹. However, during the observations presented here, typical powers observed after adjustment varied from 30 mW to 50 mW at

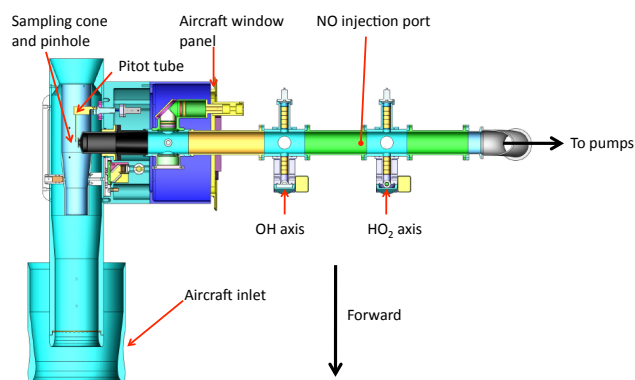


Fig. 2. Fluorescence cell for the sequential detection of OH and HO₂. OH is detected in the first axis, with fluorescence collected perpendicular to the laser beam and sample flow. NO is then injected to titrate HO₂ to OH and the signal due to HO₂ is detected in the HO₂ axis with fluorescence collection also perpendicular to the laser axis and sample flow.

$\lambda \approx 308$ nm. Dielectric coated beam splitting mirrors split the UV beam before launching the light into fibre optic cables (Oz Optics) in the ratio 60%:36%:4% for use within the OH and HO₂ axes and the reference cell respectively. Upon exiting the fibre optic cable, the laser beam entering each detection cell is collimated and baffled before intersecting the air sample. After traversing the excitation region, the beam exits the cell through another baffled arm and is directed (via a 45° mirror) into a calibrated UV photodiode (UDT – 555UV, Optoelectronics), allowing real-time measurement of the laser power. The measured laser power is used to normalise the fluorescence signal for fluctuations in laser power.

2.3 Fluorescence detection

In the fluorescence cell (Fig. 2), the UV fluorescence is collected and passed through an interference filter (Barr Associates ~50% transmission at $\lambda=308$ nm, FWHM ca. 5 nm centered at $\lambda=308$ nm). A back reflecting mirror (CVI Optics) improves the signal collection efficiency. The fluorescence signal is then focused onto the Channel Photomultiplier (CPM) (Perkin-Elmer 943P, $\sim 5 \times 10^8$ gain), where the electron pulses generated from a single photon are counted with a photon-counting card (PMS 400, Becker and Hickl). To prevent saturation, the CPM is turned off by a high voltage switching circuit (“gating box”, designed and built in-house) from the time the laser is triggered until ~ 60 ns after the laser pulse (FWHM=35 ns). The use of a temporal gating allows sensitive measurement of the fluorescence emitted from the electronically excited OH and discrimination against laser scattered light.

2.4 Reference cell

The wavelength of the laser is changed by a stepper motor, which controls the angle of the diffraction grating within the Ti:Sapp laser cavity. The absolute wavelength of the second harmonic of the Ti:Sapp ($\lambda \approx 462$ nm) is monitored by a wavemeter (Wavemaster 33–2650, Coherent). However, the resolution of this wavemeter (precision ± 0.001 nm, accuracy ± 0.005 nm) is insufficient to locate the OH Q₁(2) rotational line ($\lambda=307.995$ nm). The reference cell facilitates scanning over and identification of the Q₁(2) peak. With the reference cell maintained at low pressure (~ 3 Torr), humidified cabin air is passed over an electrically heated 80:20 Ni:Chrome filament, producing OH radicals by pyrolysis of water vapour (Stevens et al., 1994; Wennberg et al., 1994). The reference cell receives 2–3 mW ($\sim 4\%$) of the total UV radiation. The OH fluorescence signal is filtered and focussed onto a CPM perpendicular to the laser beam. The resulting signal is recorded using a photon-counting card. Because of the high concentration of OH radicals produced in the reference cell, discriminating the OH fluorescence signal from the background laser scatter does not require gating of the CPM.

Figure 3 shows the signal observed in the OH, HO₂ and reference cells during a measurement cycle on a flight on August 8th, 2006. The OH signal in the reference cell is typically 12000 cts s^{-1} above the laser scatter background of approximately 4000 cts s^{-1} . The first 25 points on the figure show the OH fluorescence while scanning over the Q₁(2) rotational line of OH to locate the wavelength of the peak fluorescence (*finding line*: from $\lambda=307.990$ nm to $\lambda=308.000$ nm). Points ~ 25 –375 in OH and reference cells show the *online* fluorescence signal (and background) as the laser wavelength is tuned to the peak of fluorescence. In the HO₂ cell, no fluorescence signal is observed until the injection of NO to titrate HO₂ to OH (points 85–375). Points ~ 375 –450 show the fluorescence as the laser wavelength is tuned to a wavelength which does not induce fluorescence in order to measure the background signal (*offline*).

The signal in the reference cell varies with aircraft cabin pressure due to changes in the laser wavelength. The variation in the wavelength generated by the laser is due to the changing refractive index of the cabin air with pressure compared with the material of the laser grating. This change in wavelength away from the maximum of the OH transition results in the signal due to OH fluorescence varying with cabin pressure. Independent of this laser wavelength change with pressure, fluctuations in cell pressure will also alter the instrument sensitivity. While the effect of changing cell pressure on sensitivity can be determined by calibration, it cannot be decoupled from changes in wavelength during AMMA as the Ti:Sapp laser cavity was not kept at constant pressure, so only data recorded on level flights (with constant laser wavelength) are considered.

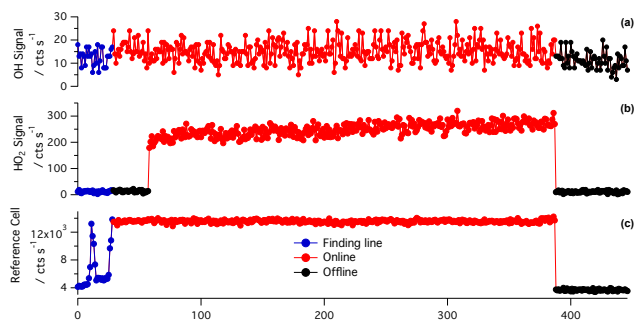


Fig. 3. The raw signal observed in the (a) OH (cts s⁻¹), (b) HO₂ (cts s⁻¹) and (c) reference cell (cts s⁻¹) for a measurement cycle during a flight on 8 August 2006. The Q₁(2) rotational line is scanned over (“finding line”, points 1–25, blue). Online (points ~25–375, red) represents the online measurement period. Offline (points 375–450, black) represents the background signal to be removed in the analysis. A 2.2% (1 σ) variation in reference signal is observed online.

2.5 Data analysis

The laser is operated at a pulse repetition frequency of 5 kHz and the contribution of the solar and dark counts (CPM thermal noise) to the observed signal is determined for each laser pulse. The fluorescence signal is collected for 1 μs (Gate A). After a 5 μs delay the non-laser background signal is recorded for 20 μs (Gate B) and the signal solely due to OH fluorescence and laser background, Sig_{fl}, is calculated:

$$\text{Sig}_{\text{fl}} = \text{SigA} - \frac{\text{SigB}}{20}, \quad (2)$$

where SigA (cts) is the number of counts in the 1 μs collection Gate A (cts s⁻¹) and SigB is the number of counts in the 20 μs collection gate (typically 0 or 1 cts s⁻¹). The total signal, Sig_{fl} (cts), is then recorded at 1 Hz and normalised for laser power (P, mW). For OH, the normalised offline signal OH Sig_{offline} is subtracted from the normalised online signal OH Sig_{online}, leaving the signal solely due to OH (OH Sig (cts s⁻¹ mW⁻¹)):

$$\text{OH Sig} = \text{OH Sig}_{\text{online}} - \text{OH Sig}_{\text{offline}} \quad (3)$$

As shown in Fig. 3, HO₂ Sig is the difference in normalised online signal observed with NO injected (HO₂+OH) and without NO added (OH only). The concentration of OH is then calculated using the experimentally determined instrument sensitivity (C_{OH}, cts s⁻¹ mW⁻¹ molecule⁻¹ cm³):

$$[\text{OH}] = \frac{\text{OH Sig}}{C_{\text{OH}}} \quad (4)$$

The concentration of HO₂ is calculated using the experimentally determined instrument sensitivity HO₂ (C_{HO₂}, cts s⁻¹ mW⁻¹ molecule⁻¹ cm³):

$$[\text{HO}_2] = \frac{\text{HO}_2 \text{ Sig}}{C_{\text{HO}_2}} \quad (5)$$

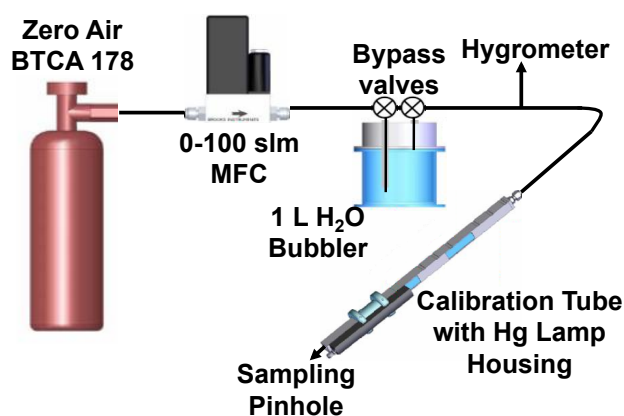


Fig. 4. Schematic representation of the calibration system. Zero air is humidified and passed through the calibration tube, where it is photolysed to produce a known concentration of OH and HO₂.

2.6 Calibration

Before and after deployment, the instrument sensitivity was determined over the range of cell pressures experienced during the AMMA campaign (between 1.5 and 2.1 Torr, equivalent to 2–2.8 hPa) using a method similar to that employed by Faloon et al. (2004) and Martinez et al. (2010). Pinholes with diameters between 0.65 and 0.85 mm were used to obtain cell pressures between 1.5 and 2.7 Torr (2–3.6 hPa) respectively.

By varying the current supplied to a low-pressure mercury lamp, a range of concentrations of OH and HO₂ were produced from the photolysis of water in humidified air (constant [H₂O]) at λ=184.9 nm:

$$[\text{OH}] = [\text{HO}_2] = [\text{H}_2\text{O}] \sigma_{\text{H}_2\text{O}} \phi_{\text{OH}} F \delta t \quad (6)$$

where σ_{H₂O} is the absorption cross-section of water at λ=184.9 nm (7.14±0.2×10⁻²⁰ molecule⁻¹ cm²; Cantrell et al., 1997a), φ_{OH} and φ_{HO₂} are the photodissociation quantum yields of OH and HO₂ respectively (=1), F is the photon flux of the mercury lamp (photon cm⁻² s⁻¹) at λ=184.9 nm and δt is the residence time in the photolysis region.

Figure 4 shows the experimental set-up of the calibration system. A known flow (ca. 50 slm: L min⁻¹ at standard temperature and pressure) of ultra high-purity air (BTCA 178, BOC Special Gases) is introduced into the system, with a variable fraction of the flow diverted (through bypass valves) to a bubbler containing distilled water in order to humidify the air. After mixing, most of the calibration gas passes through a 30 cm long black-anodised square (1.27 cm×1.27 cm) aluminium tube, where the gas is photolysed by the λ=184.9 nm emission of a mercury lamp of known actinic flux (see below) to produce equal concentrations of OH and HO₂ before delivery to the FAGE sampling point. Immediately prior to the air entering the calibration tube, a small flow is diverted to a dew-point hygrometer

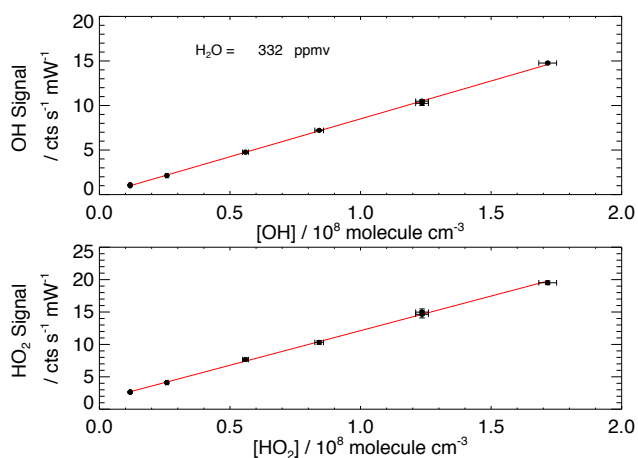


Fig. 5. Multipoint calibration for OH and HO₂ at a constant water vapour (332 ppmv). Calibrations were conducted for a range of water vapour mixing ratios between 10 000 ppmv and 332 ppmv. The lamp current was varied to produce a range of OH and HO₂ concentrations from 1×10^7 to 1.7×10^8 molecule cm⁻³. Error bars indicate the standard deviation of the data within each data point.

(CR4, Buck Research Instruments) to measure the concentration of water vapour in the flow. There are three 3.81 cm Suprasil[®] windows separated by equal distance down the length of the calibration tube. At high flow rates through the calibration tube, the gas was found to have a uniform velocity profile consistent with turbulent flow. The mercury lamp is housed in a nitrogen-purged aluminium casing, and usually mounted over the window closest to the exit of the calibration tube. This purged housing is heated to maintain a stable lamp temperature (± 1 °C), while the nitrogen flow prevents both ozone formation within the housing and absorption of radiation by ambient water vapour and oxygen prior to the light entering the calibration tube. The lamp is collimated using thin walled tubes (3 mm diameter, 8 mm length) packed together in front of the lamp. These tubes are used to create a more uniform actinic flux in the photolysis region.

Prior to calibration, the lamp flux at $\lambda=184.9$ nm was determined by N₂O actinometry through the generation of a quantifiable mixing ratio of NO from the photolysis of 10% N₂O in air. The theory and method of this technique has been described extensively in previous publications (e.g. Edwards et al., 2003; Faloon et al., 2004; Glowacki et al., 2007; Whalley et al., 2007). Two corrections were made in the calculation of the flux, F . In the NO_x analyser (Thermo Electro 42C; detection limit/precision ~ 50 pptv) used to measure the NO produced, the introduction of high concentrations of N₂O results in the reporting of artificially low NO mixing ratios. This is due to increased quenching of the electronically excited NO₂ fluorescence by N₂O within the analyser. The effect of this quenching was characterised and the corrected NO mixing ratios were calculated. The second correc-

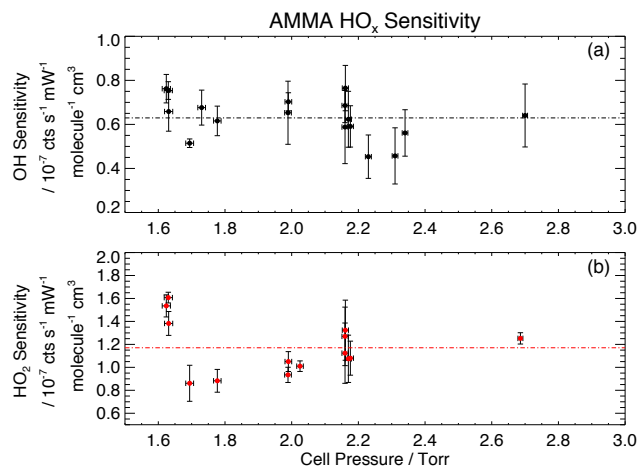


Fig. 6. Instrument Sensitivity as a function of fluorescence cell pressure for OH (a) and HO₂ (b). During AMMA, the cell pressure varied between 1.5 Torr (9 km altitude) and 2.1 Torr (sea level). The dashed line indicates the mean sensitivity used for the AMMA dataset ($C_{\text{OH}} = 0.63 (\pm 0.095) \times 10^{-7}$ cts s⁻¹ mW⁻¹ molecule⁻¹ cm³ and $C_{\text{HO}_2} = 1.17 (\pm 0.23) \times 10^{-7}$ cts s⁻¹ mW⁻¹ molecule⁻¹ cm³).

tion accounted for absorption of the light flux by N₂O across the width of the photolysis area (Edwards et al., 2003). A linear relationship between the lamp current supplied to the lamp and the flux was observed after corrections, allowing the lamp current to be varied to generate various concentrations of HO_x.

Calibrations were conducted over a range of water vapour mixing ratios from 330 ppmv to 10 000 ppmv (parts-per-million, 10^{-6} mol mol⁻¹). Figure 5 shows a typical calibration for the lowest water vapour used (332 ppmv). The instrument sensitivity to OH is a function of water vapour in the gas flow (Smith et al., 2006) due to quenching of electronically excited OH by the water vapour. Using a constant concentration of water vapour during calibrations ensures a linear relationship between the observed signal and concentration of OH or HO₂.

Over the pressure range observed in the fluorescence cell during AMMA, the sensitivity of the instrument did not vary significantly (Fig. 6) and the mean sensitivities of the instrument to OH and HO₂ were determined ($C_{\text{OH}}=0.63 (\pm 0.095) \times 10^{-7}$ cts s⁻¹ mW⁻¹ molecule⁻¹ cm³ and $C_{\text{HO}_2}=1.17 (\pm 0.23) \times 10^{-7}$ cts s⁻¹ mW⁻¹ molecule⁻¹ cm³). The calibration coefficients for a given pressure before and after the campaign were found to be within 5%, well within the calculated uncertainty. While in-flight calibrations were not possible during the AMMA campaign, instrumentation to allow calibration during flight is currently being developed. The instrument sensitivity to OH is half that of HO₂ and is due to a higher loss of OH compared to HO₂ on the surface of the cell between sampling and detection.

2.7 Limit of detection

It is possible to calculate the instrumental Limit Of Detection (LOD) for OH and HO₂ by carrying out a t-test between an observed concentration and zero concentration (0 molecule cm⁻³), assuming the variance in the background is constant throughout the measurement cycle and is represented by the variance in the offline measurement. For unequal sample sizes (online and offline), the minimum detectable HO_x, Sig_{min}, for a given confidence interval can be calculated:

$$\text{Sig}_{\text{min}} = T_{\text{CI}} \sqrt{\frac{1}{n} + \frac{1}{m}} \sigma_{\text{bg}} \quad (7)$$

where T_{CI} is the T value for a given confidence interval ($T_{69\%}=1$), n and m are the sample sizes online and offline respectively defined by the sampling frequency and σ_{bg} is the standard deviation of the background, which is assumed to be representative of the standard deviation of the background signal during the online sample. Previous studies have assumed the background signal obeys Poisson statistics (Stevens et al., 1994; Faloon et al., 2004; Martinez et al., 2010) and thus:

$$\sigma_{\text{bg}} = \sqrt{(S_{\text{lb}} + S_{\text{sb}} + S_{\text{dc}})} \quad (8)$$

where S_{lb} is the signal due to laser scatter, S_{sb} is the signal due to solar background and S_{dc} are the dark counts of the CPM.

Sig_{min} is converted into a minimum detectable concentration of OH (and HO₂) by:

$$[\text{OH}_{\text{min}}] = \frac{\text{OH Sig}_{\text{min}}}{C_{\text{OH}} P} \quad (9)$$

$$[\text{HO}_2 \text{ min}] = \frac{\text{HO}_2 \text{ Sig}_{\text{min}}}{C_{\text{HO}_2} P} \quad (10)$$

where C_{OH} and C_{HO_2} are the instrument sensitivity to OH and HO_x (cts s⁻¹ mW⁻¹ molecule⁻¹ cm³) respectively and P is the laser power in the cell (mW). Using a confidence interval of 69% (T value=1), a limit of detection is calculated for each measurement cycle (~5 min).

Table 1 shows the OH and HO₂ LODs calculated for a typical measurement cycle during the the final flight of the AMMA aircraft campaign (August 2006). During the campaign the mean OH LOD was 7.1×10^5 molecule cm⁻³ and the mean HO₂ LOD was 7.5×10^5 molecule cm⁻³ for a one minute integration time. In order to improve sensitivity to HO₂, the time between laser trigger and fluorescence collection is shortened, compared to that set for OH, which increases the background signal (and therefore σ_{bg}) and hence limit of detection but will also increase the sensitivity to HO₂. This shortened delay time is suitable for HO₂ observations, as a typical concentration of HO₂ in the atmosphere is around two orders of magnitude greater than the calculated LOD.

Table 1. Limit Of Detection (LOD) for a 60 s integration calculated for a typical run on 17 August 2006.

Parameter	OH	HO ₂
$T_{69\%}$	1	1
P/mW	10.7	5.7
C_{HO_x} (10^{-7} cts s ⁻¹ mW ⁻¹ molecule ⁻¹ cm ³)	0.63	1.17
m	60	60
n	60	60
$\sigma_{\text{bg}}/\text{cts s}^{-1}$	8.1	33.9
$[\text{HO}_x]_{\text{min}}$ (10^6 molecule cm ⁻³)	0.8	1.6

During AMMA, the performance of the YAG laser was degraded during flight due to an increase in cabin temperature, which often increased from 15 °C to 35 °C during a flight. The reduced power output from the YAG resulted in the Ti:Sapphire laser taking longer to reach the lasing threshold. The time delay between the laser trigger and the laser pulse was found to increase by several tens of ns during a given flight, an increase large enough to increase the laser background signal and affect both the sensitivity of the instrument to HO_x and the instrumental limit of detection. As the background is recorded at the end of the measurement cycle, it is possible that an increase in background signal throughout a measurement cycle could also lead to a slight underestimation of the OH concentration.

Since the AMMA campaign, a diagnostic system coupling a fast photodiode (Hamamatsu, S6468) to an oscilloscope (Waverunner LT372, Le Croy) has been developed to monitor the timing of the CPM gate trigger relative to the laser pulse and not the laser trigger. This technique allows the time between the laser pulse itself and the CPM gate trigger to be adjusted automatically in flight every 10 s, thus maintaining a constant time delay. A similar system is now used in the Leeds ground-based FAGE instrument and is described in detail in Whalley et al. (2009). Using this system, the sensitivity of the instrument to the time interval between the laser pulse and the fluorescence collection was investigated. Figure 7 shows how the background signal increases dramatically as the time between the laser pulse and fluorescence collection decreases and more of the laser pulse is detected. The limit of detection is also shown to worsen with at shorter time intervals (Fig. 7).

Under normal operating conditions (delay of 60 ns), the instrumental LOD for OH ($\sim 7 \times 10^5$ molecule cm⁻³) is below peak concentrations of OH observed in the tropics (e.g. [OH]= 9×10^6 molecule cm⁻³ observed at a tropical marine site in summer, Whalley et al., 2009). However, as the delay time decreases, the LOD becomes comparable to ambient concentrations of OH. Ambient concentrations of HO₂ are much greater than the HO₂ LOD (e.g. [HO₂]= 6×10^8 molecule cm⁻³, Whalley et al., 2009)

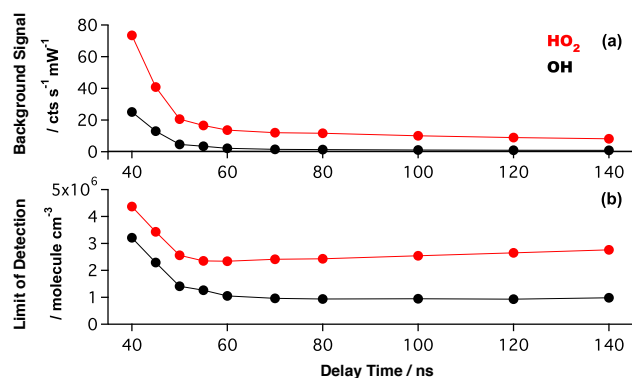


Fig. 7. Typical instrument performance for OH (black) and HO₂ (red) changes with the time interval between laser trigger and fluorescence collection. **(a)** Background signal (cts s⁻¹ mW⁻¹) and **(b)** Limit of Detection (molecule cm⁻³).

and the relative increase of HO₂ LOD compared to ambient concentrations has far less of an impact than for OH.

2.8 Instrumental uncertainty

During AMMA, water vapour ranged from 300 ppmv at altitudes above 4 km to almost 30 000 ppmv on occasion in the boundary layer. In the laboratory during ground calibrations, the impact of humidity on the calibration coefficient of the aircraft FAGE instrument was determined. For water vapour mixing ratios between 500 ppmv and 10 000 ppmv, changes of 11% and 9% were observed for C_{OH} and C_{HO₂} respectively. Although the mixing ratio of water vapour was observed on occasion to be higher than this during AMMA, calibrations of other configurations of FAGE instruments up to 20 000 ppmv in Leeds have not observed a significant further change in the calibration sensitivity beyond 10 000 ppmv.

The influence of temperature on the calibration coefficient has not been systematically characterised. However, the distance between the sampling pinhole and the fluorescence cell inside the aircraft (50 cm for the OH cell) should allow sufficient time for enough collisions to ensure equilibration to the temperature within the aircraft. In an earlier configuration of a ground-based FAGE instrument (similar nozzle diameter), the rotational temperature of the hydroxyl radical was measured as a function of distance between the sampling pinhole and the laser-excitation axis (Creasey et al., 1997). Following substantial cooling due to expansion within a supersonic jet, the temperature rose to close to ambient at the Mach Disk, followed by a slight cooling before reaching ambient again at ~20 cm. The first fluorescence cell (OH) is 50 cm from the inlet, and a thermocouple placed in the gas flow between the OH and HO₂ fluorescence cells observed room temperature when the instrument was sampling laboratory air. Therefore, it is expected that the temperature within the fluorescence cells will have reached a temperature close to that within the aircraft, although this has not been explicitly verified.

The instrumental uncertainty is calculated as the root-mean-square of the uncertainty in the determination of the flux (13% and includes N₂O calibration, rate constants, lamp current, etc.), the hygrometer (1%), absorption cross-section of H₂O (2.8%), flow controller error (1%), excitation peak location (5%), laser power reading (3%), the fit to the multi-point calibration (9% for OH and 6% for HO₂), the standard error in the fit in Fig. 5 (15% for OH and 20% for HO₂) and the uncertainty due to effects of humidity (12% for OH and 9% for HO₂), leading to an overall uncertainty of 25% for OH and 26% for HO₂.

2.9 Ancillary measurements

J(O¹D) data was provided by the University of Leicester. *J*(O¹D) is the combination of the upward and downward welling observations. During the campaign the downward pointing *J*(O¹D) actinometer failed and subsequent observations were scaled to the combined *J*(NO₂) observations, as described in Stone et al. (2010). Core aircraft data such as temperature, pressure, CO (Aerolaser AL5002 instrument), O₃ (TECO 49UV photometry instrument) and liquid water content (Johnson Williams Liquid Water Content probe) were provided by the Facility of Airborne Atmospheric Measurements (FAAM) (Reeves et al., 2010), PAN data were provided by the University of York (Stewart et al., 2008) and NO_x, NO_y (Stewart et al., 2008), acetonitrile and isoprene (Proton Transfer Mass Spectrometry – PTr-MS; Murphy et al., 2010) were provided by the University of East Anglia.

3 Results: observations of OH and HO₂ radicals

The Leeds aircraft FAGE instrument observed OH and HO₂ over a range of altitudes (500 m–9 km) and through various airmasses over West Africa. The observed signal was processed and the concentration of OH and HO₂ calculated using the instrument sensitivity determined by calibration, as described in Sect. 2.6. The 1 Hz mixing ratios of OH and HO₂ were calculated using the temperature and pressure recorded on the aircraft and averaged over 60 s. The 1 Hz HO₂ data were used directly in the study of HO₂ in clouds (Sect. 4.1).

HO_x observations were made on 13 flights during July and August 2006, with flights both during day and at night. Figure 8 shows the spatial distribution of HO₂ observed over West Africa during the AMMA campaign. The aircraft was based in Niamey, Niger and HO_x observations were made over barren soil in the north (Sahel region of northern Niger and Mali), over regions of forest (Benin) and out over the Gulf of Guinea to the south. An overview of the aircraft measurements can be found in Reeves et al. (2010) and an overview of the range of HO_x observations observed on various flights is shown in Table 2.

Table 2. Overview of HO_x observations during AMMA flights. Flights were conducted at various times of day and over a range of terrain from Sahel to the north to heavily forested regions to the south, as well as over the Gulf of Guinea to the far south

Date	Flight No.	Time (LT)	Location/Conditions	HO _x Data Range
21/07/2006	B217	14:30–18:30	Sahel/Soil Moisture	HO ₂ = 5–25 pptv
22/07/2006	B218	15:30–18:00	Convective outflow	HO ₂ = 2–20 pptv
25/07/2006	B219A	13:00–16:00	Forest: Afternoon	OH = 0–0.6 pptv
25/07/2006	B219B	18:30–22:00	Forest: Night	HO ₂ = 0–8 pptv
27/07/2006	B220	12:00–14:00	Forest: Noon	HO ₂ = 5–40 pptv
06/08/2006	B227	14:00–17:00	Sahel	OH = 0–0.4 pptv; HO ₂ = 5–14 pptv
08/08/2006	B228	09:00–14:30	Ocean/coastal	OH = 0–0.7 pptv; HO ₂ = 0–30 pptv
08/08/2006	B229	15:00–17:30	Lagos	OH = 0–0.5 pptv; HO ₂ = 5–20 pptv
14/08/2006	B232	05:00–08:00	Forest: Dawn	HO ₂ = 0–5 pptv
15/08/2006	B233	05:00–09:00	Forest: Dawn	HO ₂ = 0–18 pptv
16/08/2006	B234	14:30–18:00	Aircraft Intercomparison	HO ₂ = 2–23 pptv
17/08/2006	B235A	11:00–15:00	Forest: Noon	OH = 0–0.7 pptv; HO ₂ = 10–42 pptv
17/08/2006	B235B	18:30–21:00	Forest: Night	HO ₂ = 0.8–2.5 pptv

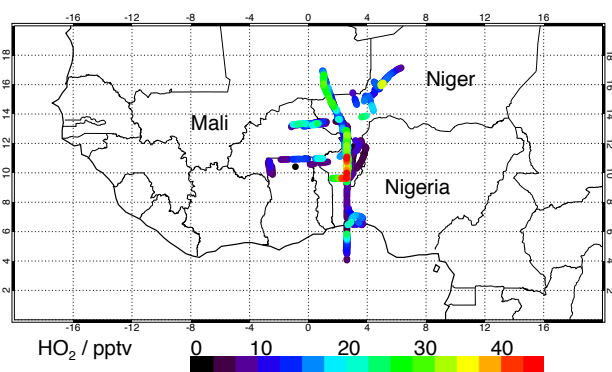


Fig. 8. Spatial distribution of HO₂ observed over West Africa during the African Monsoon Multidisciplinary Analyses (AMMA) campaign. Redder colours indicate the highest concentrations of HO₂, which were observed over the forested regions of Benin.

Figure 9 is an example of a typical OH and HO₂ time series for a flight on 17 August 2006. The aircraft sampled between 500 m and 6 km over the forested region to the north of Benin (7°–13° N). The O₃ mixing ratios were found to increase with altitude from 20 ppbv (parts-per-billion, 10⁻⁹ mol mol⁻¹) in the boundary layer to over 60 ppbv above 6 km. OH mixing ratios ranged from below the limit of detection to 0.6 pptv. HO₂ mixing ratios were found to be more variable from 5 pptv to 50 pptv on a 10 s time scale. The highest mixing ratio of both OH and HO₂ was observed at 4 km over the forested region. At the level run at 1.5 km, light cloud was encountered and HO₂ mixing ratios were found to rapidly decrease. This effect will be studied in more detail in Sect. 4.1.

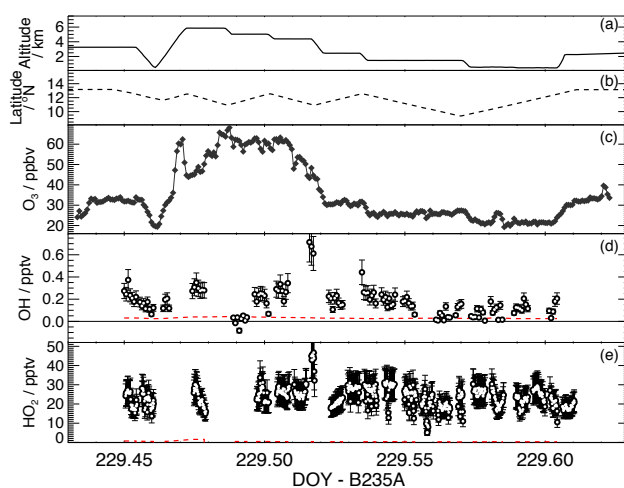


Fig. 9. Time Series of an afternoon flight from 10:40 to 15:00 UTC over the forest region in the north of Benin showing (a) altitude (km), (b) latitude (° N), (c) O₃ (ppbv), (d) OH (pptv, 60 s resolution) and limit of detection (pptv, red dashed line, 60 s resolution) and (e) HO₂ (pptv, 10 s resolution) and limit of detection (pptv, red dashed line, 10 s resolution). Error bars on OH and HO₂ indicate the instrumental uncertainty.

Overall during the campaign, the mixing ratios of OH and HO₂ were variable. Figure 10 shows the probability density function of the complete dataset of OH and HO₂ mixing ratios, with the median of the limit of detection. OH mixing ratios (Fig. 10a) from −0.27 pptv to 1.34 pptv were observed (but with very few points above 1 pptv), with a median mixing ratio of 0.17 pptv. The most frequent OH mixing ratio was observed at 0.15 pptv. HO₂ mixing ratios (Fig. 10b) varied from −0.32 pptv to 42.65 pptv, with a median mixing ratio of 7.97 pptv. 1.5 pptv was the most frequent HO₂ mixing

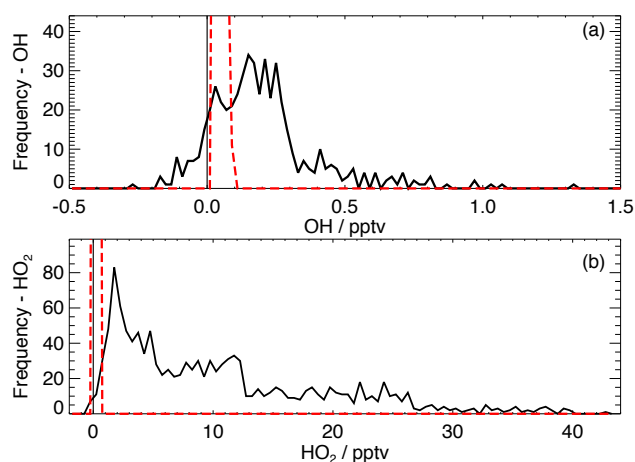


Fig. 10. Probability Density Function (PDF) of 60 s averaged observations (solid black lines): (a) OH, bin size of 0.02 pptv (b) HO₂, bin size of 0.5 pptv. PDF of limits of detection (red dashed lines).

ratio observed. For significant periods, the OH observations were close to the limit of detection of the instrument. This was due to problems with the instability of the timing of the fluorescence detection (as discussed in Sect. 2.7). However, as most HO₂ is well above the limit of detection, conclusions can be drawn with more confidence.

3.1 Diurnal variation

Although complex mechanisms determine the in situ concentrations of OH and HO₂, daytime OH production is generally dominated by the photolysis of ozone and the subsequent reaction of O(¹D) with water and often exhibits a strong diurnal profile (Rohrer and Berresheim, 2006). Figure 11 shows the diurnal profile of the entire dataset of OH and HO₂ radicals as a function of local solar time. Both OH and HO₂ were highly variable throughout the day, with the maximum OH mixing ratio (~1 pptv) coinciding with solar noon, while maximum HO₂ mixing ratio (~40 pptv) occurred shortly after solar noon. Mixing ratios of HO₂ up to 9 pptv with a mean of 3 pptv were observed at night. The observations of HO₂ at night will be discussed in detail in Sect. 4.2.

3.2 HO_x observations as a function of altitude

Figure 12 shows the daytime altitude profiles of (a) OH, (b) HO₂ and (c) the HO₂/OH ratio for data between 09:00 and 15:00 LT (Local Time), with the median value for a given 500 m altitude bin also shown.

OH mixing ratios (binned for 500 m altitude bins up to 6 km) are highly variable but the median OH is relatively constant with altitude at about 0.2 pptv, except for a large increase at the top of the boundary layer at 2 km to 0.7 pptv and distinct decrease at 5 km to less than 0.05 pptv. These observations of OH fall within the range of previous OH mea-

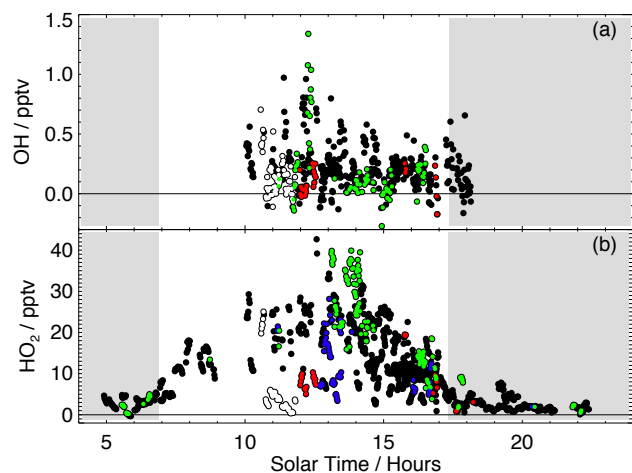


Fig. 11. Diurnal variation of (a) OH (pptv) and (b) HO₂ (pptv). Shaded areas indicate night. Specific data discussed in the text is highlighted: green points indicate high isoprene, red points are data identified as biomass burning, blue points indicate cloud sampling, white points highlight data high altitude data collected on flight B228.

surements. Observations over the mid-latitude and tropical Pacific Ocean found that median OH was relatively constant with altitude at ~0.1–0.2 pptv, increasing from ~0.1 pptv below 2 km to ~0.2 pptv at 7 km (INTEX-B and PEM-Tropics-B campaigns, Mao et al., 2009; Tan et al., 2001, respectively). Over continental mid-latitudes, median OH was again relatively constant at all altitudes but at a slightly higher mixing ratio at ~0.2–0.3 pptv (INTEX-A campaign, Ren et al., 2008). However, boundary layer OH mixing ratios varied significantly from 0.01–0.6 pptv. Observations over a tropical forested region (GABRIEL campaign, Martinez et al., 2010) found much higher OH mixing ratios with median OH increasing from ~0.4 pptv in the boundary layer, peaking at 0.75 pptv at 3–4 km and dropping to ~0.25 pptv at 8 km.

HO₂ mixing ratios were also variable at all altitudes and median HO₂ varied between 5 and 30 pptv for 500 m altitude bins up to 7 km. The lowest observed mixing ratios of HO₂ were found within 500 m of the forest surface, but the highest HO₂ mixing ratios were observed between 500 m and 1 km above the forest. At altitudes above 6 km, individual HO₂ data points varied from below the limit of detection to over 30 pptv HO₂, with a median value of ~5 pptv. Previous observations of HO₂ generally show a decrease with altitude in all locations. Over the mid-latitude North Pacific HO₂ steadily decreased from ~20 pptv at 2 km to ~7 pptv at 10 km (INTEX-B campaign, Mao et al., 2009), while over continental mid-latitudes, median HO₂ steadily decreased from ~30 pptv near the surface (ranging from ~2–60 pptv) to ~10 pptv at 10 km (INTEX-A campaign, Ren et al., 2008) and over tropical rainforests median HO₂ was

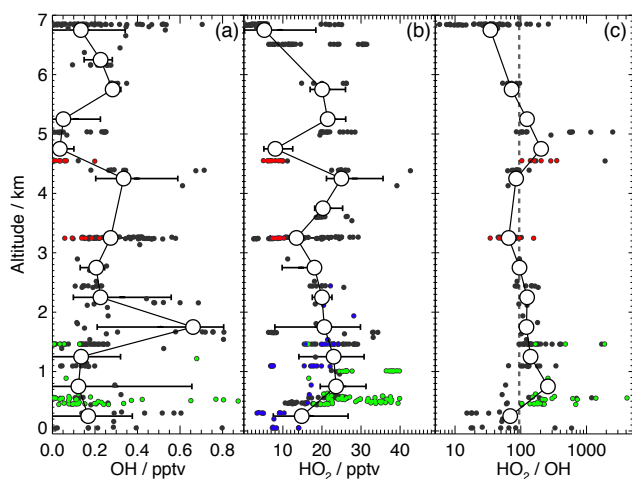


Fig. 12. Median altitude profile of (a) OH (pptv, black), (b) HO₂ (pptv, black) and (c) HO₂/OH ratio for data between 09:00 and 15:00 UTC. Median values in 500 m altitude bins are shown as large joined circles, with error bars indicating one standard deviation from the mean. The median HO₂/OH ratio of 95 is shown as a grey dashed line. 60 s data are shown as small black dots, with specific data discussed in the text highlighted: Green points indicate high isoprene, red points are data identified as biomass burning, blue points indicate cloud sampling, white points highlight data high altitude data collected on flight B228.

found to decrease from ~40 pptv in the boundary layer to ~10 pptv at 8 km (GABRIEL campaign, Martinez et al., 2010). However, observations over the tropical south Pacific Ocean show a slightly different profile; HO₂ increased from ~10 pptv at the surface to ~20 pptv at 3 km before steadily decreasing again with altitude to ~5 pptv at 11 km (PEM-Tropics-B campaign, Tan et al., 2001).

The HO₂/OH ratio was highly variable at all altitudes, ranging from 5 to 5 000 with a median value of 95. While HO_x production is dominated by O₃ photolysis, the cycling between OH and HO₂ is closely related to the abundance of CO and NO present (Ehhalt, 1999). At the altitudes considered here, overall O₃ varied between 10 ppbv and 100 ppbv and median values gradually increased with altitude to 7 km. CO varied between 50 ppbv and 450 ppbv, but overall decreased slightly with altitude (Reeves et al., 2010). Median NO varied from 100 pptv in the boundary layer to 10 pptv up to 5 km, while total NO_x was relatively constant with altitude between 100 pptv and 300 pptv (Stewart et al., 2008).

3.3 Steady state calculations

As discussed earlier, the photolysis of ozone in the presence of water vapour is the main production pathway of OH in the unpolluted troposphere (Eq. 1). Figure 13 shows the correlation between OH and $P(\text{OH})$. OH mixing ratios were highly variable with only ~11% of this variability explained by the variability in $P(\text{OH})$. In contrast to this work, previ-

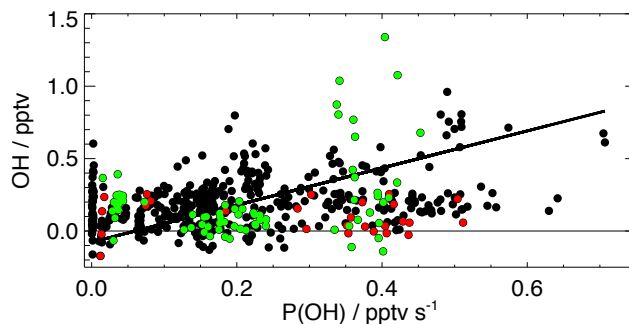
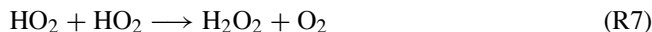


Fig. 13. Correlation between OH (pptv) and $P(\text{OH})$ (pptv s⁻¹): slope = 1.28 (±0.06) s; intercept = -0.1 (±0.01); $R^2 = 0.11$. Green points indicate observations in the boundary layer with isoprene greater than 300 pptv. Red points indicate observations within a biomass burning plume with acetonitrile higher than 250 pptv.

ous observations at ground sites with relatively constant OH sinks, found that the observed variation in OH was largely explained by corresponding variations in $P(\text{OH})$ (Rohrer and Berresheim, 2006).

In a clean air mass, the production of HO₂ is closely linked to $P(\text{OH})$ and the loss is dominated by the HO₂ self reaction:



Assuming this production of HO₂ (~ $P(\text{OH})$) and loss of HO₂ through self-reaction (Reaction R7) are equal, a steady state concentration, HO₂_{ss}, can be calculated:

$$\text{HO}_2 \text{ss} = \sqrt{\frac{P(\text{OH})}{2 k_{\text{R7}}}} = \sqrt{\frac{2 J(\text{O}^1\text{D}) [\text{O}_3] F_{\text{OH}}}{2 k_{\text{HO}_2 + \text{HO}_2}}} \quad (11)$$

Figure 14 shows that HO₂_{ss} reproduces 33% of the variability in the observed HO₂ and the slope of 0.62±0.02 indicates that overall HO₂_{ss} is overestimating HO₂, suggesting missing sinks of HO₂. This is not unexpected, given that the rapid loss of HO₂ by reaction with species such as RO₂ or NO₂ or other sinks of HO_x radicals such as heterogeneous chemistry. From Fig. 14, a number of distinct groups have been identified. HO₂ is generally reproduced by HO₂_{ss} in areas of high mixing ratios of isoprene (green) (Sect. 4.3). However, the HO₂/HO₂_{ss} ratio is much less for observations in a biomass burning plume, suggesting the presence of significant HO₂ sinks (Sect. 4.4). Stone et al. (2010) describe how the observed photolysis rates were generally slightly lower than the clear sky $J(\text{O}^1\text{D})$ calculated from the Tropospheric Ultraviolet and Visible (TUV) Radiation model. However, on part of one particular flight (B228, shown in white in Fig. 14) the observations exceeded the calculated $J(\text{O}^1\text{D})$ by a factor of 1.5. Thus, it is possible that the $P(\text{OH})$ calculated at this time is significantly overestimated.

This simple analysis is suitable for the examination of the overall HO_x behaviour but detailed interpretation requires a

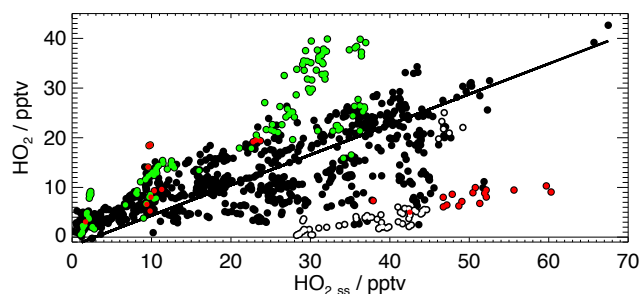


Fig. 14. Correlation between HO₂ (pptv) and HO_{2 ss} (pptv): slope = 0.62 (± 0.02); intercept = -1.75 (± 0.44); $R^2 = 0.33$. Green points indicate observations in the boundary layer with isoprene greater than 300 pptv. Red points indicate observations within a biomass burning plume with acetonitrile higher than 250 pptv. Open circles indicate observations during Flight 228, when $J(\text{O}^1\text{D})$ was significantly greater than expected. Each case is discussed in the text.

more comprehensive chemical modelling study. The detailed chemical model employed by Stone et al. (2010) was found to reproduce 55% of the variability in the observed HO₂, compared to 33% for the study here. However, the chemical model relies on the availability of ancillary data (e.g. NO) so less data points were available for comparison than used in the steady state calculation of HO_x used in this study. Due to large uncertainties and lack of coverage in the observations of OH and other key species (e.g. NO, photolysis rates), Stone et al. (2010) could not confidently compare the model to OH.

4 Discussion

A number of case studies have been identified in Sect. 3 and will now be examined in detail. A reduction in HO₂ was observed when sampling in cloud (Sect. 4.1) and HO₂ was observed at night (Sect. 4.2). Compared with $P(\text{OH})$ and HO_{2 ss}, both OH and HO₂ are enhanced in the presence of high isoprene (Sect. 4.3), but are depleted within a biomass burning plume (with acetonitrile higher than 250 pptv) (Sect. 4.4).

4.1 HO₂ in cloud

When sampling in and around clouds, HO₂ was found to rapidly decrease for short episodes, before returning to the previous higher levels again (Fig. 15). The background signal did not change when sampling around clouds, suggesting that this effect was not an instrumental artefact. Studies of a similar FAGE instrument have shown no response of the instrument sensitivity to aerosol loading (Whalley et al., 2010). Modelling studies have shown that gaseous HO₂ concentrations can be significantly reduced by aqueous phase chemistry, specifically through the efficient uptake of

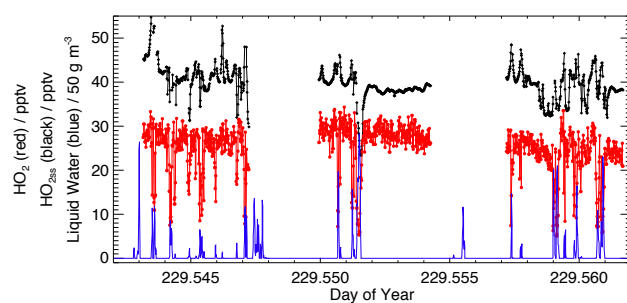


Fig. 15. Time Series of HO₂ variation in Cloud. HO₂ (1 s, pptv, red), HO_{2 ss} (1 s, pptv, black), scaled Nevzorov probe liquid water content ($\text{g m}^{-3} \times 50$) (blue). Data were taken between 13:00 and 13:30 UTC at a constant altitude of 1.5 km over northern Benin (10.9° – 12.5° N).

HO₂ onto cloud droplets (Tilgner et al., 2005). These aqueous phase models combine detailed microphysics and multiphase chemistry, but few experimental observations exist to validate the model calculated depletion of radical species in clouds. Figure 15 shows the 1 s time series of the observed HO₂, steady state calculated HO_{2 ss} mixing ratios and the Liquid Water Content (LWC, g m^{-3}) observed between 13:00 and 13:30 UTC at a constant altitude of 1.5 km over northern Benin (10.9 – 12.5° N) (Flight B235A, 17 August 2006). The timing of the short-lived reduction in HO₂ observed when sampling in cloud is reproduced by HO_{2 ss} but, as seen earlier, HO_{2 ss} is consistently greater than HO₂. Much of the variability in HO_{2 ss} is driven by changes in $J(\text{O}^1\text{D})$, which varied greatly in and out of cloud, depending on the cloud thickness. O₃ was generally found to decrease in cloud, while the fraction of O(¹D) reacting with H₂O vapour to form OH (F_{OH}) generally increased quickly due to higher water vapour, counteracting the decrease in ozone and $J(\text{O}^1\text{D})$ to an extent. Overall these fast changes in $P(\text{OH})$ resulted in reductions in HO_{2 ss}. However, the observed reduction in HO₂ was much greater than that seen in HO_{2 ss}. Thus the relative change in the HO₂/HO_{2 ss} ratio is considered for each cloud encounter, as this removes any variation due to changes in the HO_x production rates.

Figure 16a shows the 1 Hz time series of the HO₂/HO_{2 ss} ratio and the simultaneously observed liquid water content. The magnitude of the short-lived decreases in HO₂ inside the cloud are not reproduced in the calculated HO_{2 ss}, resulting in a decrease in the HO₂/HO_{2 ss} ratio. These rapid decreases in the HO₂/HO_{2 ss} ratio generally coincide with increases in liquid water and may be due to the heterogeneous uptake of HO₂ onto the cloud aerosol surface. Figure 16b shows the HO₂/HO_{2 ss} ratio as a function of liquid water content. While the values of HO₂/HO_{2 ss} ratio are highly variable, the highest ratios (median of 0.47) are found for low liquid water (below 0.2 g m^{-3}), and the lowest ratios (median of 0.25) are found for higher liquid water content (greater than 0.2 g m^{-3}).

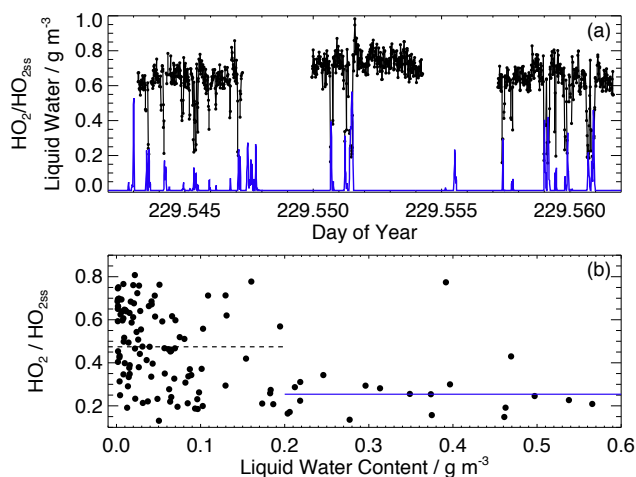


Fig. 16. (a) Time Series of HO₂/HO_{2,ss} ratio (black) and liquid water (blue); (b) HO₂/HO_{2,ss} ratio as a function of liquid water (g m⁻³). The median HO₂/HO_{2,ss} ratio is 0.4 and is shown as a dashed line.

The reduction in HO₂ in clouds has been observed previously using both FAGE and CIMS instruments (e.g. Mauldin et al., 1999; Olson et al., 2004), and this loss of HO₂ has been attributed to heterogeneous uptake of HO₂ onto the cloud aerosol. During the TRACE-P (Transport and Chemical Evolution over the Pacific) campaign, Olson et al. (2004) found that the observed HO₂ was much lower than that calculated by a comprehensive chemistry model, especially within clouds. For each 1 min data point, observations *within cloud* were identified. The observed-to-modelled HO₂ ratio was found to significantly reduce when sampling clouds with an increased liquid water content but appeared to be independent of the duration of cloud sampling. The time resolution of many species required to calculate HO₂ in chemical models is too low to interpret the short-lived depletions in HO₂ observed during AMMA (e.g. minimum 15 s for isoprene observed by PTR-MS). Therefore these rapid reductions in HO₂ are unlikely to provide any more than a qualitative sense of the heterogeneous uptake of HO₂ by cloud droplets.

The impact of HO₂ loss due to uptake on liquid cloud was investigated. The first order loss to surfaces was calculated with the diffusion of cloud droplets included (Schwartz, 1984):

$$k'_{\text{loss}} = \frac{A}{\frac{4}{c_g \gamma} + \frac{r}{D_g}} \quad (12)$$

where k'_{loss} is the rate constant for the loss of HO₂ to cloud droplets (s⁻¹), A is the cloud droplet surface area per unit volume (m² m⁻³), γ is the uptake coefficient to liquid water, r is the droplet radius (m) and D_g is the diffusion coefficient (for cloud droplets $\sim 1 \times 10^{-6}$ m² s⁻¹, Ravishankara, 1997). The uptake of HO₂ onto cloud is not tightly constrained and the uptake coefficient is thought to vary between 0.1 and 1

(Jacob, 2000; Morita et al., 2004). The mean molecular speed of the gas, c_g (m s⁻¹) is:

$$c_g = \sqrt{\frac{8 RT}{\pi M_w}} \quad (13)$$

where R is the universal gas constant, T is the temperature and M_w is the molecular weight of HO₂.

Unfortunately no information was available on the size or number concentration of cloud droplets encountered for the observation period examined here but the HO_x observations were made over the continent of West Africa and typical continental values of cloud droplet size (10 μm) and concentration (1.5 × 10⁸ droplets m⁻³) have been assumed in the calculation of k'_{loss} (Wallace and Hobbs, 2002). The main production and loss mechanisms of HO₂ were calculated for all HO₂ data where the liquid water content was greater than 0.2 g m⁻³ and an assumed mid-range γ of 0.5.

Using these constraints, the mean rate of HO₂ loss to cloud droplets was calculated to be 4.2 × 10⁶ molecule cm⁻³ s⁻¹, slightly greater than the primary production rate (4.1 × 10⁶ molecule cm⁻³ s⁻¹) but much larger than the HO₂ self reaction (0.89 × 10⁶ molecule cm⁻³ s⁻¹). Therefore it is reasonable to assume that the uptake of HO₂ onto cloud droplets is a major sink of HO₂ within a cloud. Without the inclusion of HO₂ uptake on clouds, the mean steady state calculated HO₂ mixing ratio, HO_{2,ss}, is 35 pptv, much higher than the observed mean HO₂ mixing ratio of 10.6 pptv. It is possible to calculate a cloud-influenced HO₂ mixing ratio, HO_{2,cloud}, assuming that the primary production of HO₂ (through OH) is equal to the loss of HO₂ from both self reaction and uptake on clouds:

$$P(\text{OH}) = k'_{\text{loss}}[\text{HO}_2] + 2 k_{\text{HO}_2 + \text{HO}_2} [\text{HO}_2]^2 \quad (14)$$

With the inclusion of HO₂ uptake onto cloud droplets in the calculation of HO₂, the mean HO_{2,cloud} mixing ratio was calculated to be 8.84 pptv, in closer agreement with the mean observed HO₂ mixing ratio (10.6 pptv), than the previous steady state calculation of 35 pptv.

In order to fully understand the role of clouds on the oxidative capacity of the troposphere, a more comprehensive field study of HO₂ uptake by clouds is required. The cloud droplet radius, surface area and the concentration of droplets should be measured at the same time resolution as HO₂ observations. In parallel with field studies, laboratory studies are needed to reduce the large uncertainty in current estimates of the HO₂ cloud uptake coefficient (γ), which, at present, limits our understanding of HO₂ behaviour in clouds.

4.2 HO₂ at night

HO₂ was observed at night on a number of flights over the forested region but no HO₂ data was collected over the Sahel region or ocean at night. A maximum HO₂ mixing ratio of 9.2 pptv was observed in the hour after sunset and a median

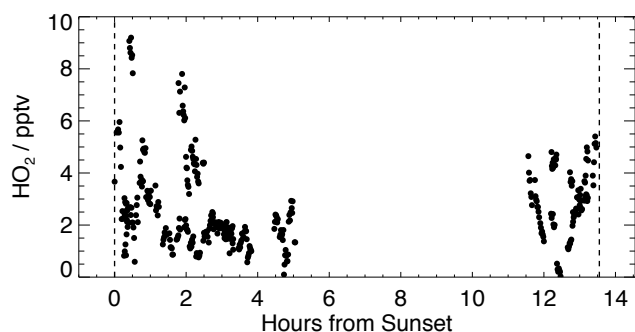


Fig. 17. HO₂ time series as a function of time from sunset. Dawn and dusk are indicated by dashed lines.

HO₂ mixing ratio of 2.2 pptv observed overall at night. Isoprene reached up to 1 ppbv at night in areas north of the most heavily forested region, with the highest mixing ratios coincident with the highest HO₂ mixing ratios. This night-time maximum in isoprene at latitudes north of the day-time maximum is consistent with transport of the air mass north with the monsoon winds (Murphy et al., 2010).

Figure 17 shows the time series of HO₂ after sunset, showing that HO₂ mixing ratios decrease as the night progresses, with the suggestion of an increase again just before dawn.

At night HO₂ can be generated from the ozonolysis of alkenes, (e.g. isoprene) and terpenes (e.g. Kroll, 2002). Isoprene emissions are strongly dependent on sunlight, unlike terpene emissions which are also a function of temperature (Guenther et al., 2006). When night-time temperatures remain high, terpene emission may continue into the night and the reaction of these alkenes and terpenes with ozone leads to the production of HO_x. Mixing ratios of HO₂ in excess of that reported here have been observed at night previously at surface sites (e.g. 1–4 pptv HO₂ was observed in mid-latitude deciduous forest (Faloona et al., 2001), up to 10 pptv HO₂ was observed on Rishiri Island, Japan, (Kanaya et al., 2002) and over 10 pptv HO₂ observed in China, Hofzuma-haus et al., 2009). However, no altitude profiles of night-time HO₂ have been reported previously.

Figure 18 shows the altitude profile of (a) HO₂ (pptv), and (b) O₃ (ppbv) observed at night. The greatest HO₂ mixing ratio observed (less than an hour after dusk) was within 500 m of the surface. O₃ mixing ratios were lowest (<20 pptv) at the surface and increased steadily with altitude through the boundary layer. Isoprene, emitted from the surface, and Methyl Vinyl Ketone (MVK), a degradation product of isoprene, were highest in the boundary layer and generally decreased with altitude. This suggests that alkene ozonolysis may play a role as a source of HO₂ at night in the forest boundary layer. Between 6 and 8 km, both isoprene and MVK were observed to increase slightly. As there is no source of isoprene at these altitudes, these species may have been convectively injected into the mid troposphere (Murphy

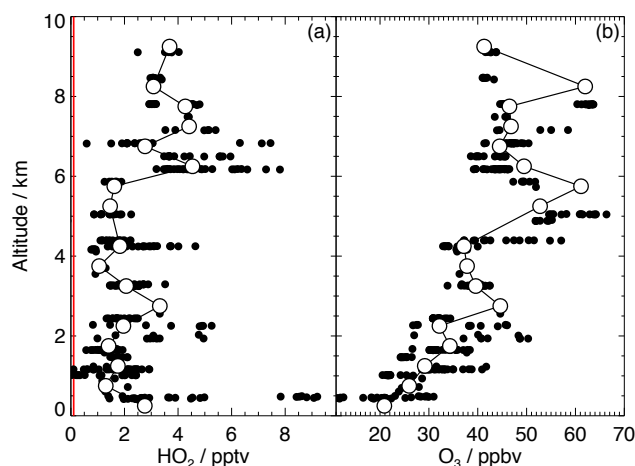


Fig. 18. Night-time Altitude Profiles of (a) HO₂ (pptv, black) and maximum HO₂ limit of detection (pptv, red) for the night-time dataset. (b) O₃ (ppbv). Median values for 500 m altitude bins are shown as white circles.

et al., 2010), resulting in the production of HO₂ at higher altitude at night.

4.3 OH and HO₂ with isoprene

Figure 19 shows the latitudinal variation of OH and HO₂ and highlights how the maximum mixing ratios of both OH and HO₂ were found in the boundary layer of the southern end of the forest region. The West African Monsoon (WAM) brings the majority of rainfall to the continent and produces a strong latitudinal gradient in vegetation and biogenic emissions such as isoprene: Murphy et al. (2010) show that the highest mixing ratios of isoprene were observed in the boundary layer above the southern forest regions (9–11° N).

Modelling studies of the latitudinal gradient of West Africa predict minimal HO_x concentrations over the forested regions due to isoprene scavenging of OH (Saunio et al., 2009). Isoprene reacts quickly with OH ($k=1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 294 K; Karl et al., 2004) and, given the concentrations of isoprene in the boundary layer above forests, this reaction should result in significant depletion of OH.

However, the observations presented here suggest that neither OH nor HO₂ mixing ratios are significantly depleted. Lelieveld et al. (2008) also observed higher than expected mixing ratios of HO_x over forests in Suriname and suggested that additional production of OH from the degradation products of isoprene (Dillon and Crowley, 2008; Peeters et al., 2009; Paulot et al., 2009; da Silva et al., 2010) could explain the high concentrations of HO_x. Given the complex nature of the oxidation of VOCs, the interpretation of these HO_x mixing ratios requires a more comprehensive modelling study than presented here. Stone et al. (2010) presents a detailed chemical box modelling study, based on the Master Chemical

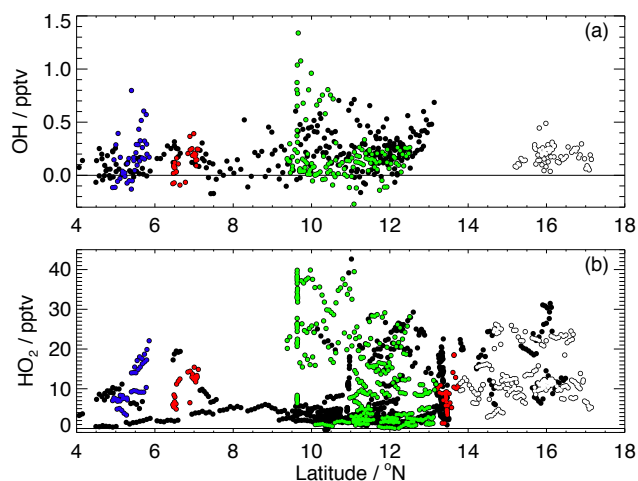


Fig. 19. Latitudinal variation of (a) OH and (b) HO₂ mixing ratio. Observations in the boundary layer are shown for data collected above the Sahel (13.75°–18° N, white), Forest (7.3°–13.2° N, green), Ocean (4°–6° N, blue) and Urban areas (6°–7.3° N and 13.2°–13.75° N, red). Observations in the free troposphere in all regions are shown in black.

Mechanism (Saunders et al., 2003), to explore the interpretation of the HO_x observations presented here.

4.4 Biomass burning plume

As shown in Figs. 13 and 14, OH and HO₂ sampled in a biomass burning plume showed some of the largest disagreement for the steady state calculations. The two distinct biomass burning episodes identified in Fig. 14 are from 22 July and 8 August 2006. The data from 8 August (observed HO₂ < calculated HO₂) is examined in more detail as there are more observations of both HO₂ and other data available. There is no NO_x data available for the five data points identified as biomass burning on 22 July (observed HO₂ > calculated HO₂).

During the 8 August episode, the biomass burning plume was sampled at two altitudes over the Gulf of Guinea. At an altitude of 4–5 km, the mean O₃ mixing ratio was 50 ppbv and the mean CO mixing ratio was 150 ppbv. At an altitude of 3.5 km, mixing ratios of O₃ and CO were some of the highest observed during the campaign (100 ppbv and 300 ppbv respectively). Coincident with these observations was a sharp increase in NO, acetonitrile (CH₃CN) and Peroxyacetyl Nitrate (PAN). Acetonitrile has been identified as a tracer for air masses affected by biomass burning (de Gouw et al., 2003).

Figure 20 shows the time series of O₃, CO, OH and *P*(OH) and HO₂ and HO_{2,ss}. The biomass burning plume was sampled at two altitudes, with the highest concentrations of both O₃ and CO observed at an altitude of 3–4 km (indicated as BB between the blue dashed lines). Within the plume at

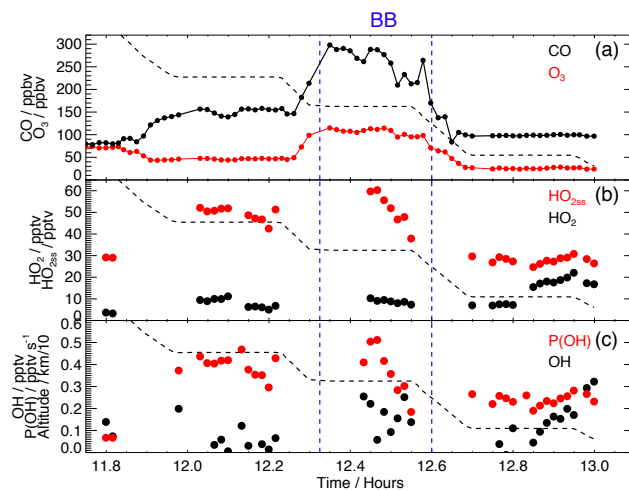


Fig. 20. Time series within and around a biomass burning (BB) plume with (a) CO (ppbv, black), and O₃ (ppbv, red), (b) HO₂ (pptv, black) and HO_{2,ss} (pptv, red), (c) OH (pptv, black) and *P*(OH) (pptv s⁻¹, red). On all graphs altitude is indicated by a black dashed line. All data are averaged to 60 s.

3.5 km, mixing ratios of 400 pptv CH₃CN (up from 100 pptv outside the plume), 600 pptv PAN (up from 50 pptv outside the plume) and 200 pptv NO (up from 50 pptv outside the plume) were observed. Between 4.5 km and 3.5 km, NO mixing ratios were found to increase from 150 pptv to 200 pptv, which is consistent with an increase in the observed OH at the lower altitude. The calculation of HO_{2,ss} does not incorporate the loss of HO_x through reactions such as RO₂+HO₂, OH+VOC, OH+NO₂ or reactions with aerosols, so it is not surprising that HO_{2,ss} is significantly higher than the observed HO₂.

Previous observations of VOCs within aged biomass burning plumes (de Gouw et al., 2003) found that the OH inferred from the degradation of species such as benzene and toluene was a factor of 4 lower than that calculated by a OH climatology model (Spivakovsky et al., 2000). While Forberich et al. (1996) measured reduced levels of OH in a biomass burning plume on one afternoon, a systematic observation of oxidation in biomass burning plumes would help in our understanding of these events. Little biomass burning takes place in West Africa during the monsoon wet season. Within the plume, NO mixing ratios reach a maximum of 200 pptv (NO₂ observations were not available at this time), while PAN mixing ratios increased to over 600 pptv, suggesting that the biomass burning plume was transported from the Southern Hemisphere (Thouret et al., 2009; Liousse et al., 2010).

In this plume, HO₂ mixing ratios are much lower than HO_{2,ss}, as expected as HO_{2,ss} does not include all possible HO_x loss processes. The reaction of OH with CO forms HO₂, thus conserving the HO_x budget. However, the reaction of OH with any of the VOCs enhanced in this plume

does not immediately form HO_x and results in localised HO_x depletion. The mixing ratios of a number of VOCs were observed to be greatly increased within the plume compared to outside the plume. Within the plume the greatest increase was observed in acetylene (factor of 7.5), followed by methanol (4.2), acetonitrile (3), benzene (2.9), ethane (2.9) and acetone (2.4). The CO mixing ratio increased from a mean of 98 ppbv outside the plume to 245 ppbv within the plume. The rate of production of HO₂ from the OH reaction with CO can be compared to the rate of production of RO₂ through the reaction of OH with VOCs.

The reactivity of OH with various VOCs can be estimated as a fraction of the OH reactivity with CO:

$$R_{\text{VOC}} = \frac{\sum_i k_i [\text{VOC}]_i}{k_{\text{CO}} + \text{OH}} [\text{CO}] \quad (15)$$

where k_i is the rate constant for the reaction of the VOC_{*i*} with OH and $\sum_i k_i [\text{VOC}]_i$ is the sum over all the products of the VOC concentration and the appropriate rate coefficient for the reaction of OH with the VOC in question. From this ratio, the impact of enhanced VOC concentrations on OH can be examined. The VOC/CO ratio was found to be 1.6 times higher within the plume (71) than outside (43), consistent with the observed HO_x depletion within the plume.

5 Conclusions

The Leeds aircraft FAGE instrument successfully measured tropospheric OH and HO₂ over west Africa during the summer monsoon in 2006. The instrument was deployed aboard the BAe-146 research aircraft as part of the African Monsoon Multidisciplinary Analyses (AMMA) campaign. For calibrations, known concentrations of HO_x were generated by the photolysis of water vapour by a mercury lamp, with the lamp flux determined by NO actinometry. The instrument sensitivity did not change appreciably over the pressure range observed in the fluorescence cell during the campaign (1.5–2.1 Torr). The mean instrumental limit of detection observed during the campaign was 7.1×10^5 molecule cm⁻³ for OH (60 s integration time) and 7.5×10^5 molecule cm⁻³ for HO₂ (60 s integration time).

HO_x observations were made during 13 flights, ranging from 50 m to over 9 km. The aircraft sampled air over the Sahel (18° N), forest (8°–12° N) and over the ocean (4° N). OH and HO₂ mixing ratios show a diurnal profile but were highly variable. Observations of OH and HO₂ were compared with steady state calculation of HO_x and differences highlighted a number of case studies. HO₂ data recorded at 1 Hz showed evidence of rapid reductions in the observed HO₂ in and around cloud, which could not be explained by changing primary production rates within the cloud. The heterogeneous uptake of HO₂ onto the cloud surface was included in the steady state HO_x calculation and improved the

agreement with the observed short-lived reductions of HO₂ in cloud. However, a more comprehensive field study of HO₂ and the properties of cloud droplets is required to fully understand the role of clouds on the oxidative capacity of the troposphere. Mixing ratios of HO₂ of 9 pptv were observed at night and the first altitude profile of HO₂ at night is presented. Up to 7 pptv of HO₂ was observed above 6 km, consistent with the convective uplift of HO₂ precursors such as isoprene. High mixing ratios of OH and HO₂ were observed in areas of high isoprene, in sharp contrast to the depletion calculated by models. Within a biomass burning plume, HO_x was found to be depleted. Calculations show that OH was 1.6 times more likely to react with VOCs than CO, resulting in the observed depletion of HO_x.

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