

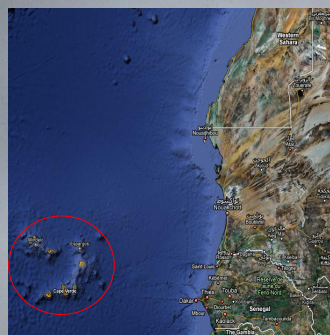
# MEASUREMENTS OF OH AND HO<sub>2</sub> RADICALS AT A TROPICAL MARINE

## LOCATION AS PART OF THE SOLAS SEASONAL OXIDANT STUDY

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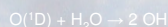
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### 1. Introduction

Field measurements of the short-lived radical species OH and HO<sub>2</sub> (referred to collectively as HO<sub>x</sub>) are vital for our understanding of the oxidative capacity of the Earth's atmosphere. Such observations are used to validate atmospheric chemical models, in particular as a means of testing our current understanding of the complex chemical processes that occur in the troposphere. Reliable measurements of HO<sub>x</sub> in tropical regions, where the warm, humid conditions lend themselves favourably to the generation of OH radicals through



are important as it has been estimated that the majority of tropospheric methane is oxidized in this region.<sup>1,2</sup> However, there have been no long-term study of the seasonal variation of HO<sub>x</sub> in the tropics.

Laser-induced fluorescence (LIF) (section 2) has been used to sensitively detect HO<sub>x</sub> radicals in the field by several groups worldwide and at a variety of locations.<sup>3</sup> This poster presents field measurements of HO<sub>x</sub> at the Cape Verde Atmospheric Observatory (CVAO, ~ 17°N, 24°W) using LIF taken over the course of this year as part of the Seasonal Oxidant Study (SOS) (section 3). The observations made during the summer study (SOS2) are compared with LIF measurements made during a similar period in 2007 (see section 4), and comparisons are made with the model predictions of [HO<sub>x</sub>] for the first two campaigns (section 5).

### 2. LIF Detection of OH and HO<sub>2</sub>

The OH radical is detected by on-resonance (at 308 nm) LIF carried out at low pressures (< 4 Torr). The low pressure extends the fluorescence lifetime of OH sufficiently to allow discrimination (in time) between the fluorescence and laser pulse. The HO<sub>2</sub> radical is converted to OH by titration with NO and detected by the same method.

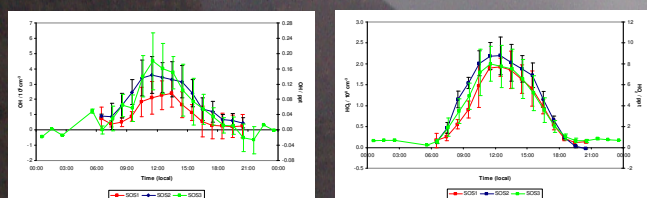
The radicals were detected *in situ* from the roof of a standard shipping container converted into a temporary mobile laboratory. Air is drawn into the low pressure cells via pin-hole nozzles, the laser beam passes perpendicular to the air stream and the fluorescence is imaged, along a 3<sup>rd</sup> axis, onto the photocathode of a channel photomultiplier.

The sensitivity of the instrument is determined as regularly as possible by a calibration method that allows the generation of known concentrations of HO<sub>x</sub>. Typical instrumental conditions for the three campaigns (SOS1—3) are shown in the right-hand table, as well as the average peak values of J(O<sup>1</sup>D), measured using a radiometer.

	SOS1	SOS2	SOS3
Dates	27 <sup>th</sup> Feb – 8 <sup>th</sup> Mar	6 <sup>th</sup> – 16 <sup>th</sup> June	1 <sup>st</sup> – 15 <sup>th</sup> Sep
Days of OH/HO <sub>2</sub>	10	11	11
LOD OH (S/N=1)	3 × 10 <sup>5</sup> cm <sup>-3</sup>	3 × 10 <sup>5</sup> cm <sup>-3</sup>	7 × 10 <sup>5</sup> cm <sup>-3</sup>
LOD HO <sub>2</sub> (S/N=2)	6 × 10 <sup>5</sup> cm <sup>-3</sup>	5 × 10 <sup>5</sup> cm <sup>-3</sup>	7 × 10 <sup>5</sup> cm <sup>-3</sup>
Average peak J(O <sup>1</sup> D) / s <sup>-1</sup>	2.6 × 10 <sup>-5</sup>	3.5 × 10 <sup>-5</sup>	3.2 × 10 <sup>-5</sup>

\* Campaign-averaged calibration factors were used

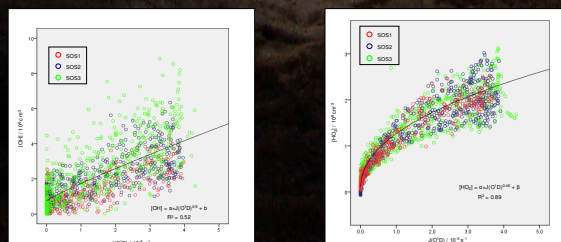
### 3. Seasonal observations of OH and HO<sub>2</sub>



Plots showing the hourly averages of OH and HO<sub>2</sub> for each of the three campaigns; the error bars are the 1σ of the hourly-averaged data and represent the day-to-day variance in the concentrations. Local time = GMT – 1:00.

Interestingly, the seasonal trend in OH is similar to that observed in [HO<sub>2</sub>+RO<sub>2</sub>] by the Leicester PERCA instrument (see the poster 'Seasonal comparison of the peroxy radical in the eastern tropical Atlantic boundary layer', Karunsalam *et al.* at the Wednesday session).

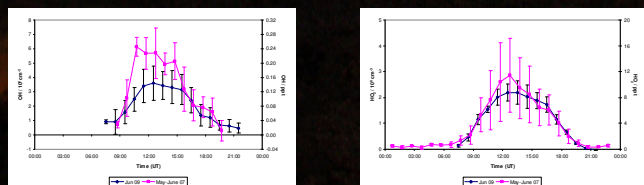
The figures below show how the concentrations of OH and HO<sub>2</sub> behave as a function of J(O<sup>1</sup>D). The power values are close to 1 for OH (suggesting the reaction J(O<sup>1</sup>D) + H<sub>2</sub>O is controlling [OH]) and 0.5 for HO<sub>2</sub> (i.e. [HO<sub>2</sub>] is being constrained by its self-reaction).



Plots of [OH] and [HO<sub>2</sub>] as functions of J(O<sup>1</sup>D).

### 4. Comparison with RHAMBLE 2007

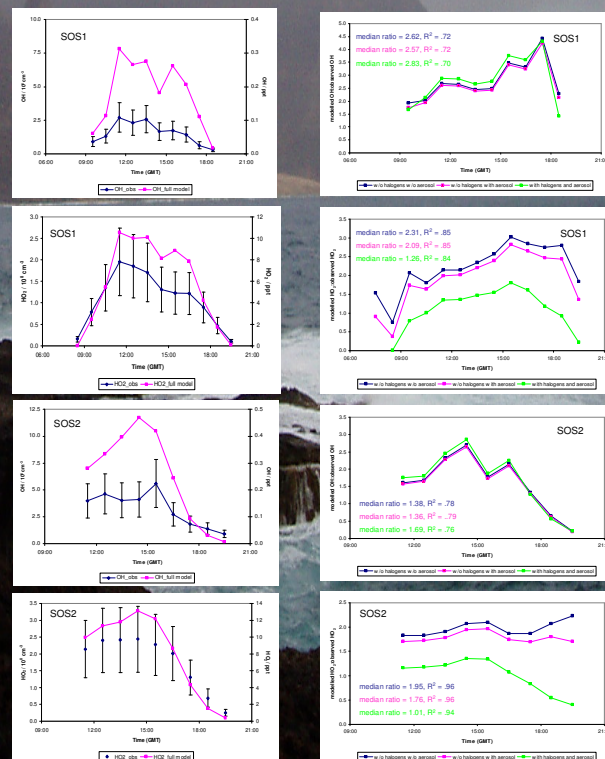
There appears to be excellent agreement between the observed concentrations of HO<sub>2</sub>, but the noontime average [OH] was lower in SOS2 compared to 2007.



Plots showing the hourly-averaged concentrations of OH and HO<sub>2</sub> from SOS2 and those measured during RHAMBLE; the error bars are the standard deviation of the daily values of [OH] and [HO<sub>2</sub>].

### 5. Modelling studies of SOS1/2

- BrO and IO levels set constant to 5ppt, when included
- Aerosol losses of other halogen species and HO<sub>x</sub> included



Plots of the mean diurnal observed and model-predicted HO<sub>x</sub> for SOS1/2 are shown on the left-hand side; the error bars represent the 2σ errors on the calibrations. Plots of the mean diurnal modelled:observed HO<sub>x</sub> are shown on the right-hand side; the median and R<sup>2</sup> values are over all points for each campaign, not the hourly averages.

### 6. References and Acknowledgements

- 1 Lawrence *et al.*, *Atmos. Chem. Phys.*, 2001
- 2 Bloss *et al.*, *Faraday Discussions*, 2005
- 3 Heard and Pilling, *Chem. Rev.*, 2003
- 4 Whalley *et al.*, *Atmos. Chem. Phys. Discuss.*, 2009

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