MEASUREMENTS OF OH AND HO\textsubscript{2} RADICALS AT A TROPICAL MARINE LOCATION AS PART OF THE SOS SEASONAL OXIDANT STUDY

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1. Introduction

Reliable measurements of OH and HO\textsubscript{2} (collectively known as HO\textsubscript{x}) in tropical regions, where the warm, humid conditions lend themselves favourably to the generation of OH radicals through the reaction of O\textsubscript{3} with water vapour

\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HO}_2 \]

are important for accurate predictions of future climate change. For radiatively-important species such as methane, CH\textsubscript{4}, the primary oxidation pathway is via reaction with OH. In fact, it has been estimated from field measurements of CH\textsubscript{4} that the majority of tropospheric CH\textsubscript{4} (98%) is oxidized between 30\degree N and 30\degree S, with as much as 25% of the total occurring in the marine lower troposphere.\textsuperscript{1,2} A seasonal study of the variation of HO\textsubscript{x} in the tropics would allow a better understanding of the oxidizing capacity in that region, leading to a more accurate prediction of seasonal CH\textsubscript{4} lifetimes in the troposphere and, in turn, long-term climate trends on a global scale.

This paper presents the first long-term, seasonal measurements of HO\textsubscript{x} made at the Cape Verde Atmospheric Observatory (CVAO) using sensitive laser-induced fluorescence (LIF) spectroscopy taken as part of the Seasonal Oxidant Study (SOS), compared with LIF measurements made during a similar period in 2007 (see section 3), and comparisons are made with the model predictions of [HO\textsubscript{x}] for the SOS1 and 2 (section 4).

2. LIF Detection of OH and HO\textsubscript{2}

The OH radical was detected by on-resonance (at \approx 308 nm) LIF carried out at low pressures (\textless 4 Torr). The low pressure extended the fluorescence lifetime \(P_{\text{th}}\) of the HO\textsubscript{x} radicals through the reaction of O(\textdagger) with HO\textsubscript{x}, where the warm, humid conditions lend themselves favourably to the generation of OH radicals (collectively known as HO\textsubscript{x}). The low pressure extended the fluorescence lifetime \(P_{\text{th}}\) of the HO\textsubscript{x} radicals through the reaction of O(\textdagger) with HO\textsubscript{x}.

The radicals were detected in situ from the roof of a standard shipping container converted to a temporary mobile laboratory. Air was drawn into the LIF pressure cells via pinhole nozzles, the laser beam passed perpendicular to the air stream and the fluorescence was imaged, along a 3\degree axis, onto the photocathode of a gated channel photon multiplier.

The sensitivity of the instrument was determined in the field at Cape Verde as regularly as possible by a calibration method that allowed the generation of known concentrations of HO\textsubscript{x}. Typical instrumental conditions for the three campaigns (SOS1—3) are shown in the right-hand table, as well as the average peak values of [JO(D)] = 6 x 10\textsuperscript{-10} measured using a radiometer.

3. Seasonal observations of OH and HO\textsubscript{x}

Figure 1 shows that a total of 31 days of HO\textsubscript{x} measurements were made during 2009, excluding periods when the instrument was not performing within acceptable tolerances and when measurements were influenced by bad weather or local conditions. OH showed the greatest day-to-day variation, with concentrations over 10\textsuperscript{15} molecule cm\textsuperscript{-3} observed on two days in SOS1. SOS3 was characterized by very unstable weather, which may explain why the levels of both HO\textsubscript{x} were so variable. The mean levels of HO\textsubscript{x} were relatively consistent over the three mini-campaigns (see Figure 2).

The peaks are proportionally larger than those observed in the summer of 2009,\textsuperscript{7} although they do agree within the 2\sigma confidence bands dictated by the errors in the respective calibrations and are not statistically different. Both OH and HO\textsubscript{x} tend towards zero concentration at night, although the number of night-time measurements during SOS was restricted.

In the only previous long-term study of OH behaviour, Rohe and Berresheim were able to show that a 5-year dataset of [OH] in Germany could be simply described by the equation\textsuperscript{1}

\[ \text{[OH]} = (a \times \text{[JO(D)]}) + c \]

Our values of [OH] show a reasonable correlation with [JO(D)] with a value of 0.9 close to 1 (see Figure 3), suggesting that the levels of OH are heavily influenced by the reaction of O(\textdagger) with water vapour. HO\textsubscript{x} shows a very good correlation with [JO(D)], with a close to 0.8, suggesting that its concentration is controlled by its self-reaction.

Figure 2. Average diurnal from 2007 and 2009 (hourly averaged data).

The error bars symbolize the 2\sigma confidence limits of the calibrations.

Figure 3. Plots of concentration against [JO(D)] for each HO\textsubscript{x} species. The lines represent the nonlinear fit to the data described by the equations.

Figure 4. Comparison of observed [HO\textsubscript{x}] with model predictions.

Figure 5. Averaged diurnal modelled-to-calculated [HO\textsubscript{x}].

5. References and Acknowledgements


The authors would like to acknowledge Dr James Lee and Dr Katie Read (Univ. York) for the core data used in the models, Prof. Lucy Carpenter (York) for co-ordinating the Seasonal Oxidant Study, and Bruno Faria, Luis Mendes and Gisela Duarte for their logistical assistance in Cape Verde. We would also like to thank Dr Andrew Goddard and the staff of the technical workshops at the School of Chemistry, Leeds, for their continued support. The Cape Verde Atmospheric Observatory is part of a bilateral German-UK initiative to undertake long-term ground- and ocean-based observations in the tropical Eastern North Atlantic Ocean region. It links with the international programme SOLAS, the EU-funded TROPOS-Atlantic Eastern North Atlantic (SOS2) Observatory project, and with the German BMBF-funded Sunbird Project in the Arctic observing project.