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Measurements of OH and HO2 at a tropical marine location as part of the SOLAS Seasonal Oxidant Study

Stewart Vaughan (1), Trevor Ingham (1), Daniel Stone (1,2), Lisa Whalley (1), Mathew Evans (2), and Dwayne Heard (1)

(1) School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK. (s.vaughan@leeds.ac.uk), (2) School of Earth and Environment, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK.

The hydroxyl radical, OH, is the dominant daytime oxidant in the troposphere, particularly in the tropical marine boundary layer, where the warm, humid conditions and high solar incidence lend themselves favourably to the formation of OH. Chemical models show that the majority of atmospheric methane is oxidised in tropical regions so that accurate measurements of OH in those regions are crucial for our understanding of the global oxidizing capacity, especially in terms of climate change. However, there are few published measurements of OH, and also of HO_2, which is closely coupled to OH, in such environments.

Long-term measurements of HO_x (OH and HO_2) using FAGE (Fluorescence Assay by Gas Expansion) were made at the Cape Verde Atmospheric Observatory (16.85°N 24.87°W), on the island of São Vicente, as part of the Seasonal Oxidant Study (SOS) in the tropical Atlantic during three distinct seasonal periods; SOS1 during February—March (generally dry with clear sky), in June during SOS2 (clear and dry), and SOS3 in September (some sustained periods of heavy rainfall). Preliminary data analysis suggests mean midday concentrations of OH were 3.6, 3.5 and 4.6×10^6 cm^{-3} for SOS1, 2 and 3; the corresponding mean noontime concentrations of HO_2 were 1.8, 2.1 and 1.8×10^8 cm^{-3}. Compared to measurements made in May—June 2007, during the RHAMBLE project the peak concentration of HO_2 for SOS2 seem similar, whereas the concentration of OH in SOS2 appears about 30% lower.

A chemical box model, based on the Master Chemical Mechanism (MCM) and includes halogen chemistry and heterogeneous loss of $HO_x$to aerosol surfaces, has been used to describe the diurnal behaviour of OH and HO_2 for each campaign. By assuming that the concentrations of the halogen oxides BrO and IO, key intermediates in the depletion of tropospheric ozone – an important precursor for HO_x – are similar to those observed at the observatory in 2007, the model is able to recreate well the relative diurnal trends of both OH and HO_2. A preliminary comparison shows that the model overpredicts the daytime concentrations of both HO_x-species by factors of $\sim$1.9 and $\sim$1.6 for SOS1 and SOS2, respectively, suggesting an overestimation of HO_x-sources and/or an underprediction of HO_x-sinks; modelling analysis of the data for SOS3 will take place in spring 2010. Attempts to resolve the differences between the model predictions and the measurements, including a sensitivity analysis with respect to halogen oxides, will be discussed.