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The chemistry of OH and HO_2 radicals in the boundary layer over the tropical Atlantic Ocean

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Abstract. Fluorescence Assay by Gas Expansion (FAGE) has been used to detect ambient levels of OH and HO_2 radicals at the Cape Verde Atmospheric Observatory, located in the tropical Atlantic marine boundary layer, during May and June 2007. Midday radical concentrations were high, with maximum concentrations of 9×10^6 molecule cm^{-3} and 6×10^8 molecule cm^{-3} observed for OH and HO_2, respectively. A box model incorporating the detailed Master Chemical Mechanism, extended to include halogen chemistry, heterogeneous loss processes and constrained by all available measurements including halogen and nitrogen oxides, has been used to assess the chemical and physical parameters controlling the radical chemistry. The model was able to reproduce the daytime radical concentrations to within the 1 σ measurement uncertainty of 20% during the latter half of the measurement period but significantly under-predicted [HO_2] by 39% during the first half of the project. Sensitivity analyses demonstrate that elevated [HCHO] (~2 ppbv) on specific days during the early part of the project, which were much greater than the mean [HCHO] (328 pptv) used to constrain the model, could account for a large portion of the discrepancy between modelled and measured [HO_2] at this time. IO and BrO, although present only at a few pptv, constituted ~19% of the instantaneous sinks for HO_2, whilst aerosol uptake and surface deposition to the ocean accounted for a further 23% of the HO_2 loss at noon. Photolysis of HOI and HOBr accounted for ~13% of the instantaneous OH formation. Taking into account that halogen oxides increase the oxidation of NO_x ($NO \rightarrow NO_2$), and in turn reduce the rate of formation of OH from the reaction of HO_2 with NO, OH concentrations were estimated to be 9% higher overall due to the presence of halogens. The increase in modelled OH from halogen chemistry gives an estimated 9% shorter lifetime for methane in this region, and the inclusion of halogen chemistry is necessary to model the observed daily cycle of O_3 destruction that is observed at the

surface. Due to surface losses, we hypothesise that HO_2 concentrations increase with height and therefore contribute a larger fraction of the O_3 destruction than at the surface.

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