



Comparisons between box and global model simulations of chemical oxidation in the tropical marine boundary layer

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Atmospheric oxidation processes during the daytime are dominated by the OH radical, particularly in the tropical marine boundary layer, where the warm, humid conditions and high solar irradiation lead to high OH production rates. Atmospheric models have shown that such high OH production rates in tropical regions lead to a significant fraction of global methane oxidation in tropical regions. Understanding the processes controlling OH concentrations, and thus the extent of methane oxidation, in tropical regions is therefore essential to our understanding of the global oxidising capacity and for accurate climate change predictions. Long-term measurements of OH, and the closely coupled HO₂ radical, were made using the FAGE (Fluorescence Assay by Gas Expansion) technique 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 in February–March, June and September 2009 (Vaughan et al., ACP, 12, 2149, 2012). In this paper we describe model simulations of OH and HO₂ radicals with both a heavily constrained box model using the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC), based on the Master Chemical Mechanism (MCM v3.2, extended with a halogen chemistry scheme), and the three-dimensional global chemistry transport model GEOS-Chem (v9-01-03, including recent updates to include bromine chemistry). The box model calculations indicate that solar photolysis of ozone is responsible for over 80 % of midday radical production, with photolysis of HCHO contributing a further 9 % of the total midday radical production. Radical losses at midday are dominated by CH₃O₂ + HO₂ (26 %), uptake of HO₂ onto aerosol surfaces (21 %) and HO₂ + HO₂ (18 %). Both model approaches result in an over-prediction of OH and HO₂, potentially arising from incomplete consideration of radical sinks. However, the two model approaches differ in the impacts of halogen chemistry. In the box model, halogen chemistry acts to increase OH concentrations, while in the global model halogen chemistry decreases OH. The reasons for these differences, and their implications, will be discussed.