Geophysical Research Abstracts
Vol. 12, EGU2010-3533-1, 2010
EGU General Assembly 2010

Long term measurements of NOx and O3 in the remote tropical North Atlantic marine boundary layer

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A highly sensitive instrument has been deployed to measure nitric oxide (NO) and nitrogen dioxide (NO2) at the Cape Verde Atmospheric Observatory in the remote tropical North Atlantic marine boundary layer (MBL). Using two different methods, the instrument was assessed to have a detection limit of around 1.8 pptv for NO and 5.5 pptv for NO2 for hour-long integration periods. The overall accuracy was estimated at $\sim$ 18% for NO and 30% for NO2. Measurements of NO, NO2 and ozone (O3) over a period of 40 months from October 2006 show very low levels of NOx (typically < 30 pptv) and net daytime ozone destruction on most days of the measurement period. Air originating over Africa exhibited the highest levels of NOx ($\sim$35 pptv) and reduced daily O3 destruction, with O3 production observed on a few days. Air that had not originated over Africa showed lower NOx levels ($\sim$25 pptv), with greater observed O3 destruction. A dependence of the observed O3 destruction on NO mixing ratios, averaged over all air masses, was observed and reproduced using a simple box model. The model results imply that the presence of between 17 and 34 pptv of NO (depending on the month) would be required to turn the tropical North Atlantic from an O3 destroying to an O3 producing regime. The importance of the halogen oxide species IO and BrO in O3 destruction was also demonstrated by the model, with the model underestimating the O3 destruction by around 50% if the reactions of these species are emitted. Vertical profiles taken from an aircraft show that the observed O3 destruction happens throughout the boundary layer, showing that the halogen chemistry has a significant and extensive influence on photochemical ozone loss in the tropical Atlantic Ocean boundary layer. The omission of halogen sources and their chemistry in atmospheric models may lead to significant errors in calculations of global ozone budgets, tropospheric oxidizing capacity and methane oxidation rates, both historically and in the future.