Photochemistry in biomass burning plumes and implications for tropospheric ozone over the tropical South Atlantic

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J. Geophys. Res., in press, 1998

Abstract

The TRACE-A (TRansport and Atmospheric Chemistry near the Equator - Atlantic) expedition was conducted during the 1992 southern tropical dry season to evaluate the contribution of biomass burning to the seasonal ozone maximum observed off the west coast of southern Africa. The chemical composition of biomass burning emissions over source regions and over the South Atlantic were measured. To evaluate the photochemistry taking place in the plumes we examine the evolution of enhancement ratios (DY/DX, where D indicates the enhancement of a compound in the plume above the local background mixing ratio, Y is individual NMHC, CO, O3, CH4, N2O, HNO3, PAN, CH2O, acetone ,H2O2, CH3OOH, HCOOH, CH3COOH or aerosols and X is CO or CO2) as a function of plume age. We find that DCO/DCO2 decreases from 0.05 to 0.02 from regions of fresh fires to remote ocean locations as a result of photochemical loss of CO and decreasing backrgound mixing ratios of CO2. We use DO3/DCO to infer ozone production in plumes and find an increase from 0.11 to 0.95 from fresh to old plumes., Enhancement ratios in older plumes, however, must be corrected for an upwards bias due to photochemical loss of CO. Net production of O3 in aged biomass burning plumes appears to be approximately 10% of the median gross O3 production in the region. We conduct a case study of a large biomass burning plume sampled at 4-km over the course of five days off the west coast of Africa and simulate the evolution of this plume using a photochemical lagrangian plume model. We find that NOx emitted in the fire is rapidly converted to PAN. The degradation of PAN helps maintain the NOx concentration in the plume which is converted to HNO3 over the course of a week. Net ozone production in the plume is negligible, however, and is limited by the availability of NOx. Finally, we examine the influence that biomass burning plumes have on regional ozone production both by scaling up from the DO3/DCO enhancement ratio in old plumes and through the use of 0-dimensional photochemical modeling along flight tracks. We find that old plumes contribute substantially to ozone production and may be important contributors to the regional enhancement in column O3. The maintenance of NOx concentrations through the conversion of PAN to HNO3 appears to be a regional phenomenon. Using a simulated wet season calculation we find that gross ozone production rates in background air during the dry season are approximately three times larger than during the wet season.